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**Chemistry & Materials Science
Progress Report**

**Weapons-Supporting Research
and
Laboratory Directed Research and Development**

FY 1995

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April 1996

**Lawrence
Livermore
National
Laboratory**

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Contents

Weapons-Supporting Research

Atomic Site Physics and Chemistry of Uranium Hydriding	3
<i>M. Balooch, A. Hamza, W. Siekhaus, T. Gonis, and P. Sterne</i>	
High Beryllium Content Capsules for the National Ignition Facility	5
<i>R. Brusasco, S. Letts, R. Cook, P. Miller, and M. Saculla</i>	
Pulsed Positron Beam for Defect Analysis in Aged Plutonium	7
<i>Carlos A. Colmenares, Richard H. Howell, and James E. Hanafee</i>	
Large Capsule Development for National Ignition Facility Targets	9
<i>Steven R. Buckley, Gerald Wilemski, De Vu, Diana Schroen-Carey, and Bob Cook</i>	
Impurity and Laser-Induced Damage in the Growth Sectors of Rapidly Grown Potassium Dihydrogen Phosphate Crystals	12
<i>Ming Yan, Jim DeYoreo, Rich Torres, Mike Runkel, Bruce Woods, Natalia Zaitseva, and Ian Hutcheon</i>	
Kinetics of Phase Transformations in the Heat-Affected Zone of Welds	17
<i>J. W. Elmer, Joe Wong, M. Fröba, and P. A. Waide</i>	
Molecular Level Study of Shock Propagation in Damaged Triaminotrinitrobenzene	19
<i>Laurence E. Fried and Craig Tarver</i>	
Deformation Mechanisms in U-6Nb	22
<i>Gil Gallegos, Adam Schwartz, and Ed Li</i>	
Aerogel Sensor Development	24
<i>L. W. Hrubesh, J. H. Satcher, and S. R. Buckley</i>	
Mechanism of Ductile Rupture in the Aluminum-Sapphire System Elucidated Using X-Ray Tomographic Microscopy	27
<i>Wayne E. King, Geoffrey H. Campbell, David L. Haupt, John H. Kinney, Robert A. Riddle, and Walter L. Wien</i>	
Attribution Technology Program	32
<i>Ron Lougheed</i>	
Special Nuclear Materials Detection and Materials Control	33
<i>Ron Lougheed</i>	
Beryllium Fuel Capsules for the National Ignition Facility	33
<i>D. M. Makowiecki, C. S. Alford, and R. J. Wallace</i>	
Synthesis of 1,3,5-Triamino-2,4,6-trinitrobenzene and Other Insensitive Energetic Materials	38
<i>Philip F. Pagoria, Alexander R. Mitchell, and Robert D. Schmidt</i>	

Uranium and Plutonium on Metal Surfaces	42
<i>P. A. Sterne</i>	

Molten Salt Destruction of High Explosives	43
<i>B. E. Watkins, R. S. Upadhye, and R. Behrens, Jr.</i>	

Laboratory Directed Research and Development, Exploratory Research

Giant Magnetoresistance Materials with Novel Spacer Layers	49
<i>A. Chaiken and R. Michel</i>	

Atomic Force Microscopy of Solution-Grown Crystals	53
<i>T. A. Land, J. J. De Yoreo, A. J. Malkin, Yu G. Kuznetsov, and A. McPherson</i>	

Matrix-Assisted Laser Desorption-Ionization: Using Time-of-Flight Mass Spectrometry to Identify Biological Molecules	58
<i>Donald Eades and Hugh Gregg</i>	

A Novel Approach to SiC Film Production for Micromechanical and Electronic Components	60
<i>Alex Hamza, Mehdi Balooch, and Dino Ciarlo</i>	

Isotope Measurements for Innovative Groundwater Management	62
<i>G. Bryant Hudson</i>	

Meso-Structural Features in High-Tc Superconducting Materials Using Pair Distribution Function Analysis of Neutron-X-Ray Scattering Data	63
<i>George H. Kwei</i>	

Superplasticity in Aluminum Alloys	67
<i>T. G. Nieh</i>	

Bonding and Structure of Nanocrystalline Thin Films	69
<i>Louis J. Terminello</i>	

Selenium Isotope Geochemistry	71
<i>Alan Volpe and Brad Esser</i>	

Enhanced Nuclear Stability	74
<i>John F. Wild, Ronald W. Loughheed, and Kenton J. Moody</i>	

Laboratory Directed Research and Development, Director's Initiative

Multilength-Scale Modeling: Crystal-Plasticity Models in Implicit Finite-Element Codes	79
<i>David D. Sam and Wayne E. King</i>	

Molecular Level Studies of Energetic Materials	81
<i>C. Souers, F. Foltz, Larry Fried, Jim Belak, Jon Maienschein, and Choong-Shik Yoo</i>	

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Weapons-Supporting Research

Atomic Site Physics and Chemistry of Uranium Hydriding

M. Balooch, A. Hamza, W. Siekhaus, T. Gonis, and P. Sterne

This project is a combined experimental-theoretical study of the nature of the physical changes and the underlying chemical and physical basis for hydriding uranium. We used temperature-programmed desorption (TPD), molecular beam mass spectrometry (MBMS), and atomic force microscopy (AFM) to study the early stage of hydriding.

Temperature-Programmed Desorption

The surface is dosed with molecular or atomic hydrogen at room temperature to perform TPD experiments. The duration and effective pressure of the dose specify the exposure at the surface. The sample is then heated at a constant rate. As a result, hydrogen molecules desorb from the surface and are detected by a mass spectrometer. Analysis of the TPD results provides the sticking probability, binding energy, and saturation coverage of hydrogen on uranium. The initial sticking probability for dihydrogen on clean uranium can be estimated by the ratio of the coverage as measured by TPD to the exposure of the surface to dihydrogen. For the lowest coverage measured, the initial sticking probability is about 4×10^{-2} . The sticking probability decreases rapidly with hydrogen coverage. The apparent sticking probability at a coverage of 9×10^{13} molecules/cm² is an order of magnitude lower than the initial sticking probability. An estimate of the uranium atoms on the surface from the uranium nearest neighbor distance is 1.3×10^{15} atoms/cm². Assuming dihydrogen dissociates into atomic hydrogen on the surface, an apparent saturation coverage occurs at about 0.15 ML (ML = hydrogen atoms/uranium atoms).

Molecular Beam Mass Spectrometry

A beam of molecular hydrogen is directed toward the surface to perform MBMS experiments. Simultaneously, the surface is exposed to deuterium by a doser close to the surface. Recombination on the surface produces HD molecules that subsequently desorb and are measured by the mass spectrometer. In

addition, the reflected dihydrogen signal is monitored as the surface is cleaned by argon ion bombardment. The decrease in the reflected dihydrogen signal is the measure of the total reaction probability. The difference between the total reaction probability and the HD signal is a measure of the hydride formation probability.

Figure 1 shows the reaction probabilities for the clean and oxidized surface. The isotopic natural abundance of deuterium in hydrogen is about 1.5×10^{-4} ; therefore, the HD signal for the oxidized surface is mainly due to the existence of HD in the hydrogen beam rather than recombination at the surface. According to Figure 1, the sticking probability of hydrogen on clean uranium is about 3×10^{-2} at room temperature (which agrees with TPD results). In addition, the hydriding probability of about 5×10^{-3} at room temperature and an effective (equivalent) hydrogen pressure of 2.5×10^{-6} Torr can be deduced from the data.

Atomic Force Microscopy

For AFM studies, a polycrystalline uranium sample is electropolished to reveal the grain boundaries. After polishing, the sample is quickly placed in ultrahigh vacuum; in the time between polishing and pump-down, the sample becomes slightly oxidized. Figure 2(a) shows an AFM image of a $0.5 \mu\text{m} \times 0.5 \mu\text{m}$ area of this surface. The crossing of two grain boundaries is seen in the image. One begins in the upper right corner and continues to the middle left side. The other begins in the bottom right corner and proceeds to the middle left side. The pressure in the chamber was then increased to 5×10^{-2} Torr for 5 min followed by evacuating the hydrogen and examining the surface morphology of the same area with AFM.

Figure 2(b) shows the image after 10 min hydrogen exposure. Raised features approximately 10 nm in diameter are observed along the grain boundaries. These features continue to grow in size with continued exposure. After 20 min of exposure, the raised features have grown to approximately 40 nm in

Figure 1. Reaction probability for H_2 (ϵ_{total}) and HD (ϵ_{HD}) vs time. The argon ion bombardment was initiated at 1-1/2 min. By 2 min, the surface oxide has been sputtered away such that the reaction is occurring on the clean uranium surface.

diameter (Figure 2[c]); however, the density of the features did not change noticeably.

We assign these raised features to the regions where hydriding has been initiated because the uranium to uranium hydride transformation involves a volume increase of a factor of 1.8. By assuming that the hydride at particular sites grows isotropically (forms a half-sphere cavity into the uranium surface,

which is filled with hydride) and the density of these sites do not change, we can calculate the total number of uranium metal atoms reacted to form hydride during each 5-min exposure. The hydride formation probability is the ratio of the number of uranium hydrides formed to the number of dihydrogen striking a unit area times 1.5 (three atomic hydrogen in UH_3 vs two in dihydrogen).

Figure 3 shows the variation of the hydride formation probability with exposure. Initially, the hydride formation probability is extremely small because the total area associated with sites that favor the hydride formation is small. In time the reactive area around the sites expands resulting in a higher reaction rate. For example, the reaction probability increases by a factor of about 5 going from 10 to 20 min, and the area around the perimeter of the hydriding sites increases by a factor of greater than 4. The rate increased by three orders of magnitude in the time studied, up to 20 min. After 20 min, stable images could not be obtained, presumably because of hydride powder mobility and interference with the AFM tip.

Calculations of the electronic structure of a clean alpha-uranium surface and a uranium surface with a hydrogen overlayer showed a minimal change in the density of states of the surface uranium atom with hydrogen coverage. The hydrogen atoms, therefore, provide too small a change in the electronic structure for them to be readily observed in an energy-dependent STM experiment.

Summary

In our study, a combination of TPD, MBMS, and AFM in vacuum has provided detail kinetic information of the interaction of hydrogen and water vapor with uranium metal. We determined the sticking probabilities of these gases to the surface, identified different binding sites and desorption energies from them, and measured the hydride formation and

Figure 2. Atomic force images of (a) clean uranium exhibiting grain boundaries from upper right to middle left and from lower right to middle left; (b) the same area after 10 min of exposure to 5×10^{-2} Torr dihydrogen; and (c) the same area after 20 min of exposure to 5×10^{-2} Torr dihydrogen.

molecular recombination probabilities. For the slightly oxidized sample, the hydriding was shown to initiate mainly at the grain boundaries. The probability of hydriding then increased by three orders of magnitude in 20 min with hydrogen exposure at 5×10^{-2} Torr. The reactivity of dihydrogen and water vapor with uranium is greatly reduced by oxidation and carburization of the uranium surface.

Publications

M. Balooch and A. V. Hamza, "Hydrogen and Water Vapor Adsorption on and Reaction with Uranium," *J. Nucl. Mater.* (accepted).

Figure 3. Hydride formation probability measured by AFM plotted as a function of hydrogen exposure in minutes at a pressure of 5×10^{-2} Torr.

High Beryllium Content Capsules for the National Ignition Facility

R. Brusasco, S. Letts, R. Cook, P. Miller, and M. Saculla

Our goals in this exploratory research project were to demonstrate the formation of a hydrocarbon-based, vapor-phase-deposited coating that incorporates a significant amount of beryllium. Such a coating would be a candidate material for fuel containers for inertial confinement fusion (ICF) implosion experiments at the National Ignition Facility (NIF). The research concept considered was to prepare coatings in the same manner used for current Nova ICF target ablaters (plasma polymerization) but to use a volatile organoberyllium precursor to incorporate a significant amount of beryllium into the plasma polymer network. To meet this goal, we modified an existing coating system originally designed to handle toxic materials; demonstrated high metal loading in such a system with a surrogate; and prepared a

beryllium-doped plasma polymer (CHBe), with appropriate characterization of its composition and an evaluation of the preparative process.

Early experiments using germanium as a surrogate demonstrated that, in fact, one could prepare plasma polymer coatings with very high metal incorporation rates.¹ Subsequent to these experiments, the diethylberyllium source material was attached to the coating system and coatings with beryllium incorporation were demonstrated.² Because all organoberyllium compounds react violently upon exposure to the air, we were concerned that the resultant beryllium-doped coating would be extremely air sensitive. This proved not to be the case, as the coatings were easily and safely handled after removal from the system. These coatings are

qualitatively very similar to plain plasma polymer in terms of appearance, color and mechanical properties. X-ray photoelectron spectroscopy (XPS) characterization of the coating shows that the beryllium-to-carbon ratio is approximately 1:1; however, the beryllium in the coating is oxidized (Table 1). There is no evidence to suggest that the beryllium is incorporated into the growing film as oxide; it is more likely that the beryllium is oxidizing upon completion of the deposition experiment and exposure to the ambient environment.

A careful analysis of the XPS data indicates that most of the oxygen in the coating is associated with the beryllium. It should be pointed out that XPS is very surface specific and may not be indicative of the composition in the bulk of the thin film.

X-ray diffraction analysis of the coating shows it to be amorphous. These data are consistent with a view that the beryllium is intimately bound to the polymer network, which kinetically stabilizes the beryllium. If the beryllium were to exist as very fine particles of zero-valent metal, one would expect much more vigorous reaction with ambient air than is observed. It is not known how far the beryllium oxidation front extends into the coating, and this point must be investigated further.

We discovered that the diethylberyllium source material is not suitable for continued development work. The vapor pressure of the material decreases with time, and experiments have indicated that thermal decomposition of the source and slow dissociation kinetics in the liquid phase are taking place. As a consequence, the deposition rates are too slow to be useful for ICF target fabrication and the experimental conditions are difficult to reproduce.

We may be able to overcome these difficulties by considering a different source material. In FY 1996, we plan to investigate the use of cyclopentadienyl-methyl beryllium (CpMeBe). This material has a high vapor pressure (24 Torr at room temperature) and is said to have an indefinite shelf life. We plan to evaluate this precursor and simultaneously investigate the oxidation front through the resultant plasma polymer by

Table 1. XPS characterization of CHBe coatings.

Element	Number of peaks	Observed energy (eV)	Composition (at.%)
Beryllium	1	115.7	27
Carbon	2	287.2; 288.5	36
Oxygen	2	534.0; 535.6	35

controlling exposure of the coating to the air. We will also explore the possibility of retarding oxidation through the use of diffusion barrier layers.

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Pulsed Positron Beam for Defect Analysis in Aged Plutonium

Carlos A. Colmenares, Richard H. Howell, and James E. Hanafee

The aging details of plutonium metal have taken on new significance as the strategy for maintaining nuclear stockpile evolves. In particular, the fate of helium produced from radioactive decay and the formation of voids caused by radiation damage have not been explored at the microscopic level. Details of the dispersion of helium in the metallic lattice and the effect that dispersion variations have on significant mechanical properties is not known. While void formation is seen at elevated temperature, there is no existing database for predicting when the increase of helium in the lattice, as a function of age, will result in microvoids that are potentially deleterious in weapons applications of plutonium. The current nuclear stockpile is up to thirty years old and the useful life of these weapons may be extended beyond fifty years, at which point the problems mentioned may become very significant.

Up to now, transmission electron microscopy (TEM) has been the only technique applied to detailed investigations of microvoids; however, its results are limited because of the difficulty of preparing adequate samples without modifying their properties. Positron lifetime analysis is an established defect analysis technique that can detect voids below the sensitivity of TEM and determine their size. Although void signatures were detected in early measurements,^{1,2} past application of this technique to plutonium problems has been limited because of less informative positron spectroscopic techniques, the low throughput of the measurements, and the restrictive sample geometry, which required surrounding a radioactive ^{22}Na source with plutonium. These difficulties have been eliminated by the development of a new positron annihilation lifetime spectrometer at LLNL.

In this report we will describe the progress made in the following areas: (1) the new positron annihilation lifetime spectrometer, (2) the encapsulation of samples for transport from the plutonium facility to Building 194, (3) the results of theoretical calculations determining the implantation distribution of positrons in the proposed container geometry, and (4) the

optimum thickness for the positron detectors and calculations predicting the positron annihilation lifetime values for plutonium and its defects.

Experimental Procedures

The new positron lifetime spectrometer, housed in Building 194, is based on a beam of thermalized positrons accelerated to up to 3 MeV by a Pelletron electrostatic accelerator and then implanted in the sample where the positrons are annihilated. Because of the advantages attained by the lifetime analysis configuration, this low-intensity, high-energy beam can be used to perform high data rate analysis by positron annihilation lifetimes. The beam geometry makes it possible to take measurements on single sample pieces. Furthermore, because the beam is penetrating, the samples may be encapsulated or covered by overlayers. Consequently, measurements on doubly encapsulated plutonium samples, of up to 8 g, can be routinely performed.

Plutonium samples of several ages will be encapsulated in all-welded Stainless Steel 316 vessels outfitted with two thin foils (0.005 in.) welded onto the front face of each container on top of each other. These containers with the plutonium samples inside are considered "sealed sources" and will be allowed to be shipped between Buildings 332 and 194, where the spectrometer is located.

We calculated the implantation of positrons in the planned geometry, the optimum positron detector thickness, and other positron transport questions using the PERK code, which is a derivative of PEREGRINE based on the EGGS charged particle transport protocol.

We performed calculations of the values of the positron annihilation lifetimes using the local density approximation and a muffin-tin orbital description of the atomic charge sites. These calculations have been validated extensively by comparison to published positron annihilation lifetime data for elements, compounds and their defects.

We located 20- and 40-year-old specimens of weapons-grade plutonium, and we are in possession of the former. We expect the older specimens within the next few months. The samples will be machined into 0.550-in.-diam discs taking care to preserve the front or back face intact for positron lifetime measurements. The 20-year-old sample has been machined to the proper size, and a procedure has been written to carry out its encapsulation. We are now waiting for approval of the encapsulation procedure to carry out the source assembly.

Results

We performed calculations and experiments to design the sample capsule and determine potentially useful configurations of beam and detectors for the lifetime measurements. We used the PERK code to determine the implantation distributions of positrons in the selected sample/holder geometry and the optimum thickness for the positron detectors, and to predict a low contribution to the lifetime spectrum from positrons that end in the encapsulating windows or sample holder.

We conducted lifetime measurements with the apparatus on metal and composite samples to determine the characteristics of the lifetime system and to obtain a preliminary placement of the detector. Detector configurations were found that have less than 1 part in 10,000 background counts from unwanted radiation. Studies to complete the optimization of these configurations while retaining high data rates are under way.

During the detector optimization studies, improvements in the accelerator (Pelletron) beam focusing were required to minimize unwanted background contributions. We determined the source of the focusing problems, and corrections are under

way. An upgrade of the beam lifetime system will be done in early FY 1996 to remedy these problems and to increase the annihilation data counting rates.

Calculations of the positron annihilation lifetimes in plutonium predict a value of 140 ps for defect-free delta-phase plutonium, 252 ps for a single atomic vacancy in delta-phase plutonium, and 500 ps for a void of 2 nm. These values are well separated and can be easily resolved in positron annihilation lifetime experiment.

We were unable to work with plutonium from the end of March to November because the plutonium facility was closed to comply with DOE-mandated changes. This severely affected our ability to get any experimental data with plutonium. During this time, we designed the encapsulation vessel and obtained agreement from the management of Buildings 332 and 194 and the health physics representative as to the suitability of the final design of the sample container. This took several meetings and many iterations of the proposed sample container, which is now considered to be a "sealed source" and can be transported between buildings. The 20-year-old plutonium specimens have been machined to size and an encapsulation procedure written to do the actual sealed-source encapsulation. As soon as we get the necessary approvals, we will proceed with the operation.

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Large Capsule Development for National Ignition Facility Targets

Steven R. Buckley, Gerald Wilemski,^{*} De Vu,[†] Diana Schroen-Carey,[‡] and Bob Cook

The National Ignition Facility (NIF), currently planned to begin operation in about 2002, will require fuel capsules roughly four times larger than the current 0.5-mm-diam capsules used on Nova.¹ Nova capsules are fabricated by first producing a thin-walled polystyrene shell, and then overcoating this *mandrel* with 40 to 50 μm of plasma polymer that forms the capsule ablator.² An important feature of Nova capsules that must be reproduced in the larger NIF capsules is an extremely smooth surface finish, especially over the relatively long wavelength surface modes. The surface roughness in the low-mode region originates with the underlying mandrel and is largely unaffected by the plasma polymer overcoating process. The current Nova-scale, thin-walled polystyrene mandrels are produced by a heated drop-tower method, and their surface quality is very high. Unfortunately, the current heated drop-tower technology is limited to mandrel sizes with submillimeter diameters; thus, a critical need for the production of NIF-scale capsules is the development of a technique for producing a 2-mm-diam shell to serve as the mandrel for NIF capsule production. The key criterion for these new, larger mandrels is that they exhibit surface smoothness similar to current Nova mandrels. This project is exploring a possible route to NIF-scale mandrels based on the use of interfacial chemical reactions.

Figure 1 shows the basic idea of this approach to large shells. Spherical droplets of a solvent containing one component (A) are suspended in a second immiscible solvent containing a second component (B). If A and B are selected so that they react to form a crosslinked and thus insoluble polymer, a solid shell will form at the interface between the two phases. Washing procedures followed by drying will yield a shell. This approach can rapidly produce many shells of the desired diameter; the key concern is the surface

finish of the shell. This can be affected by two aspects of the method. First, very low mode asymmetries, especially mode 2, can result from spherical asymmetries in the initial drop because of agitation or other perturbations to the droplet symmetry during the initial stages of interfacial reaction, when the shell "shape" is being set. Second, higher mode roughness at wavelengths of a few tens of micrometers or less can result from the reaction process itself, and thus is very sensitive to the particular chemistry employed.

In FY 1995, we focused almost exclusively on the reaction between organic solution droplets of the diacid chloride, isophthalyl chloride (IPC), and a basic aqueous solution of poly(vinylphenol) (PVP), a polystyrene-like polymer with deprotonated phenolic groups at the *para* positions on each ring. This reaction leads to the crosslinking of existing polymer molecules (PVP) at the droplet surface. This chemistry was chosen because it has been explored first by Takagi et al.³ and then at LLNL for foam shell overcoating. There are, however, a large number of chemistries that could be used, and some exploration of the amine-isocyanate chemistries that are common in industrial microencapsulation processes has been undertaken and is discussed in our complete report.

Figure 2 shows the reaction chemistry for the IPC-PVP reaction. The IPC is dissolved in an organic solvent, usually diethyl phthalate, at concentrations of a few weight percent. This solution is placed in a syringe pump that delivers droplets of controllable size into a stream of aqueous stripping solution containing surfactant additives that promote droplet stability. The droplets are carried by the stripping solution through a delivery tube into a vessel holding the aqueous PVP solution. This solution must be highly alkaline ($\text{pH} \approx 13$) to dissolve the PVP by completely reacting all of the phenolic hydrogens with OH^- to form a highly negatively charged polymer. The suspended droplets are constantly agitated by a mechanical stirrer to prevent their settling, and the polycondensation crosslinking reaction begins as soon as the stripping solution around a droplet is replaced by solution containing PVP molecules. The

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Figure 1. The interfacial method for forming shells involves the reaction of chemical components at the interface between a droplet of one phase suspended in an immiscible phase.

process is ended by rapidly flushing the mixture with distilled water. Depending on the goal of the experiment, several tens to hundreds of shells may be produced in a single batch. After several organic solvent exchanges to remove diethyl phthalate and unreacted IPC, the shells are dried in a supercritical CO_2 fluid-exchange drier.

Much of our work in FY 1995 was directed at developing the above process. Issues such as solvent and surfactant choice, density matching, droplet generator design and droplet size control, methods of agitation, effects of pH, and a number of other factors

required experimental work that we will not discuss here. We also studied the shell wall thickness as a function of reactant concentrations and time. Our objective was to determine whether it would be possible to determine conditions that would allow us to "grow" NIF-thickness ($\approx 150 \mu\text{m}$) ablators. The result of this study was that it was impossible to form walls any thicker than about $30 \mu\text{m}$ with the IPC-PVP chemistry. The study also revealed, however, that the surface finish of the shells produced could be greatly affected by the reaction conditions, and these results will be discussed below.

Figure 2. Isophthalyl chloride–poly(vinyl phenol) crosslinking reaction.

Figure 3. SEM photos of shell exteriors produced under different conditions: (a) 2 wt% PVP and 3.5 wt% IPC with a 20-min reaction time; (b) same as in (a) but with a 120-min reaction time; and (c) same as in (a) but with 10 wt% IPC.

As noted earlier, excellent surface finish over long wavelengths is key to a useful NIF-scale shell technology. Thus, our early focus was on developing procedures that produced shells with good sphericity. This was found to depend heavily on the agitation during growth and subsequent solvent exchange steps. We developed processes that give us roughly 10% of our shells with asphericity of less than 1% (major-minor axis divided by diameter). We then began to analyze the surface roughness using our atomic force microscopy (AFM)-based sphere mapper and found that some of the shells had significant roughness over all wavelengths. AFM patch scans and scanning electron microscopy (SEM) on selected shells showed a variety of surface morphologies that seemed to depend on the concentrations of the two reactants and the time of reaction. Figure 3 shows SEM photos of the exteriors of three different shells produced under different reaction conditions. Clearly, the surfaces are quite different. In contradistinction to the variation in the outside surfaces, SEM analysis showed the inside surfaces in all cases to be smooth and featureless.

In FY 1996, our focus will be to extend these preliminary observations and carefully study the relationship between surface morphology and reaction conditions with a goal of determining those conditions that produce the best surfaces. These will then have to be compared to what is needed for NIF capsules and to other possible routes to NIF-scale mandrels to determine whether the interfacial polymerization route to NIF mandrels is worth further development.

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Impurity and Laser-Induced Damage in the Growth Sectors of Rapidly Grown Potassium Dihydrogen Phosphate Crystals

Ming Yan, Jim De Yoreo, Rich Torres, Mike Runkel, Bruce Woods, Natalia Zaitseva, and Ian Hutcheon

Potassium dihydrogen phosphate (KDP) single crystals are commonly used as nonlinear optical elements for harmonic generation of laser radiation.¹ Large ($40 \times 40 \text{ cm}^2$) KDP crystals with high damage thresholds are required for high-power laser applications, such as the National Ignition Facility.² Conventionally, KDP crystals with sizes longer than 20 cm have been grown from saturated aqueous solution at growth rates of about 1 mm per day along the primary optical (z) axis. Recently, large KDP crystals have been grown successfully from highly supersaturated solution at rates exceeding 10 mm per day.³ In addition to the growth of the pyramidal faces (along the z axis), as occurs in the conventional method, rapid crystallization from highly supersaturated solution results in significant growth of prismatic faces in directions (x and y) perpendicular to the primary optical axis. Two growth sectors typically contain different levels of impurities. In this report, we summarize our efforts to correlate the optical properties of the crystals with the presence of chemical impurities in the prismatic and the pyramidal growth sectors. We also performed laser-induced damage threshold (LDT) studies on the two different growth sectors and at their boundaries both before and after thermal annealing. The results address the issue of optical performance and laser-induced damage in KDP crystals.

Ultraviolet Absorption and Impurity Analysis

Figure 1 shows the ultraviolet (UV) absorption spectra of a KDP crystal fabricated from a rapidly grown boule and cut perpendicular to the z axis. The absorption spectra were measured along the z axis and show a dramatic spatial variation because of the

impurity distribution. The central spot (Figure 1[a]) lies in the pyramidal sector, while two spots near the edge (Figure 1[b,c]) are in the prismatic sector. As the figure shows, the absorption in the pyramidal sector is much lower in magnitude than and has different spectrum from that of the prismatic sector. The spectral analysis shows that the absorption in the prismatic sectors commonly consists of bands at 200 and 270 nm. However, the relative intensities of the two bands vary dramatically with position. Figure 2 shows the absorption spectra of two plates cut from the same boule of KDP but at different heights along the z axis. The position at which the 200-nm absorption increases in magnitude is nearer to the outer edge in #5-3 than in #5-2, consistent with the shift at the pyramid-prism sector boundary position as the crystal grows taller. Therefore, the absorption at 200 nm depends primarily on the growth sector in which it is measured. However, the 270-nm absorption band (monitored at 300 nm to resolve it more fully from the 200-nm band) also depends on the relative growth rates of the crystal. Unlike the 200-nm band, whose absorption is constant in the prismatic sector, the 300-nm absorption in both plates increases monotonically with the growth rate, as shown in Figure 2. Also, the higher magnitude of both absorption bands correlates with higher impurity contamination in the crystals, as measured by inductively coupled plasma-mass spectrometry (ICP-MS), as discussed below.

Besides the critical loss of the laser intensity at the 355-nm wavelength, the UV absorption also correlates with the optical performance, such as distortion of the transmitted wavefront and birefringence loss. Figure 3 shows a comparison of the spatial profiles of UV absorption with the level of strain-induced optical birefringence as measured by depolarization loss. The

Figure 1. (a) Schematic diagram of a KDP crystal boule and the location of crystal plates measured. The open area is the pyramidal sector and the shadow one is the prismatic. The bottom shows the spatial variation in optical absorption at 250 nm (same scale as above). (b) The absorption spectra at position a, b, and c as shown at (a).

strong correlation indicates that the incorporation of impurities is one cause of optical distortion that affects the quality of crystals used for harmonic generation.

Chemical analyses using ICP-MS show that impurities in KDP are at the parts per million level. Table 1 lists analytical data for the KDP crystals referred to above. The data show that the segregation of impurities from the starting solution to the crystal is different in the two growth sectors and also depends on the identity of the individual impurities. The ratio of impurity in the prismatic and pyramidal sectors were measured by secondary ion mass spectroscopy (SIMS) analysis using a micrometer-size $^{16}\text{O}^-$ primary ion beam. Higher concentrations of aluminum, chromium, iron, strontium, yttrium, zirconium, antimony, lanthanum, and cerium were found in the prismatic sector, magnesium is enriched in the pyramidal sector, and rubidium remains relatively constant between two sectors.

The origin of the observed impurity-induced UV absorption is not yet fully understood. We found that the absorption at 200 and 270 nm is also present in the

Table 1. Impurity analysis of KDP salt and different growth factors.

Impurity ions	Starting salt (ppm)	LLNL #5-2 pyramidal (ppm)	LLNL #5-2 prism (ppm)	SIMS analysis prism vs pyramidal
Sb	3.5	0.17	12.5	150–500
Pb	0.2	0.1	0.2	—
Al	<0.6	<0.3	7	30
Fe	<0.2	<0.06	0.6	100–200
Rb	3.8	0.8	0.8	1

Figure 2. The absorption spectra of the top (#5-3), the bottom (#5-2) plate, and their growth rate as a function of position along the x direction.

Figure 3. The absorption and depolarization loss in crystal #5-2 as a function of spatial position.

starting aqueous solutions and that the absorption at 270 nm increases in the solution as the impurity level increases. Our initial intentional doping experiments show that insoluble metal phosphates have the same absorption spectrum as that observed in the starting solutions and final crystals. Such molecular impurities may be responsible for the UV absorption we measured. However, a more complete understanding of the UV absorption due to each impurity requires more experiments where the presence of impurities are individually controlled.

Laser-Induced Damage and Thermal Annealing

The damage tests were performed using the Zeus test facility with 10-Hz operation at 355 nm (3 ω) and a 7.6-ns pulse width. The damage laser fluence was typically varied from 2 to 25 J/cm² with a 1.1-mm

beam diameter. The laser-induced damage was inspected using a 100 $\times$ darkfield microscope before and after laser irradiation. In addition, a scatter diagnostic laser was used to illuminate the test site and was coaligned with the damaging beam. A charge-coupled device (CCD) camera with 10- μ m resolution was used to collect the scattered light image at 90 deg to the laser incident direction.

Figure 4 shows the results of standard LDT measurements with 600 shot exposures in the prism and pyramidal sectors. This standard test shows that the laser damage threshold is at the same level in both sectors in spite of large variations in impurity content between these two growth sectors. This observation contradicts published data that show that higher UV absorption results in a lower LDT.⁴ However, this is the first time the LDT with impurity and UV absorption variations has been measured in the same crystal. We also performed high-fluence tests on those sites

Figure 4. The laser-induced damage threshold as a function of position in (a) pyramidal and (b) prismatic sectors. Circles represent sites that survived the damage test, while crosses represent sites where we observed damage. The sites with more than one symbol were tested at low fluence before testing at high fluence.

Figure 5. Images of scattered light from pyramid/prism sector boundary before (left) and after (right) laser irradiation at 7-J/cm^2 fluence. Damage and diagnosis laser were incident at the top of the image, and the images were collected at 90° to the direction of the incident beam. The intense scattering in the images at roughly 45° angle is from the sector boundary.

that survived the initial standard test. The damage threshold increases almost two fold when the site was preirradiated. This is consistent with the laser-conditioning effect observed in earlier work.⁵

In addition, we found the LDT of the prism-pyramid sector boundary was 2 to 3 J/cm^2 , which is less than half of that in the bulk of the crystal. Figure 5 shows the light scattering from the sector boundary before and after laser irradiation. A laser fluence of 9.7 J/cm^2 caused catastrophic sector boundary damage that was a few hundreds of micrometers in size and observable by the naked eye. The preirradiation image shows intense light scattering due to the strain in the sector boundary where the catastrophic damage occurs. Furthermore, both the

sector boundary scattering and LDT were not altered by laser annealing (preirradiation).

Following the initial testing, the crystals were annealed in a vacuum oven at 160°C for approximately 120 h . After thermal annealing, the intense light scattering from the sector boundary was no longer observable and the LDT along the sector boundary increased dramatically to the same level as the LDT in the bulk of the crystal. The disappearance of light scattering at the sector boundary suggests that strain at the boundary was thermally annealed, thereby increasing its damage threshold. These observations also suggest that the laser damage occurs where there is a highly localized strain that could enhance its local E field, resulting in higher

photothermal absorption, which is one of the mechanism of laser-induced damage in some optically transparent materials. The UV absorption in the bulk of the crystal after thermal annealing was measured and remains the same as before annealing. This suggests that the UV absorption is not due to those crystal disorders that could be thermally annealed, such as those generated by irradiation. Currently, we have not been able to directly correlate impurity aggregation with damage at the sector boundary because of the spatial resolution in the measurement. The standard LDT test in the pyramidal and prismatic sectors performed after thermal annealing showed no significant increase in the LDT, in contrast to the case of 1 ω irradiation as reported in other work.⁵

Summary

We identified the impurity contamination in two growth sectors of the rapidly grown KDP single crystals. Such contamination depends on the starting materials and the growth rate. The impurities observed by absorption spectroscopy are identified as the origin of lattice distortion and anomalous optical birefringence in the KDP crystals. We also found that the laser damage threshold of highly contaminated prismatic sectors is the same as that of the much more

pure pyramidal sectors. However, the laser damage threshold at the sector boundary is less than half that of the bulk. We successfully thermally annealed the crystal defects along the sector boundary and increased the boundary LDT to the same level as in the bulk crystal.

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Kinetics of Phase Transformations in the Heat-Affected Zone of Welds

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Although welding is an enabling technology used in many industrial settings, it is least understood in terms of the phases that actually exist, the variation of their spatial disposition with time, and the rate of transformation from one phase to another at various thermal coordinates in the vicinity of the weld. With the availability of high flux and, more recently, high brightness synchrotron x-radiation sources, a number of diffraction and spectroscopic methods have been developed for structural characterization with improved spatial and temporal resolutions to enable in situ measurements of phases under extreme tempera-

ture, pressure, and other processing conditions not readily accessible with conventional sources. In this research program, we applied a unique experimental tool developed at LLNL—spatially resolved x-ray diffraction (SRXRD)—to determine the phases present and map out spatially their relative fractions in the heat-affected zone (HAZ) of fusion welds. As a central goal of this project, we plan to use the in situ phase and real-time transformation kinetic data gathered by SRXRD to develop a generalized model of HAZ phase transformation behavior. The longer range goal of this program is to apply the experimental techniques and

modeling capabilities developed here to investigate the more complex phase transformation behavior in steels where replacive and displacive transformations, second-phase particle dissolution, and grain growth all contribute to the integrity of the resulting weld.

Phase Mapping

During FY 1995, we mapped the phases that exist in the leading (heating) portion of a gas-tungsten arc (GTA) weld in commercially pure titanium using SRXRD. A 0.33-mm-diam x-ray probe generated at the Stanford Synchrotron Radiation Laboratory (SSRL) was used to observe the hexagonal close-packed (hcp) and body-centered cubic (bcc) phases that exist in the heating portion of a titanium weld HAZ. These direct observations of the low-to-high temperature phase transformation during welding were recorded for the first time, and they can be used to understand the kinetics of phase transformations in the steep thermal gradients produced during welding.

Analysis of the SRXRD data from previous SSRL runs was completed on grade 4 titanium, indicating the presence of oxygen in the HAZ caused by incomplete inert gas shielding during welding. Results of these experiments showed that the oxygen diffuses into the α -titanium crystallographic lattice, resulting in predictable shifts in the SRXRD diffraction patterns. The in situ determination of the oxidized surface layer was used to explain variations in the infrared (IR) surface emittance of the titanium welds. These data were used to assist with calibration of the IR thermography measurements made during the weld.

New Experimental Techniques

In February 1995, we demonstrated the feasibility of using imaging plates as two-dimensional x-ray detectors for our SRXRD experiments. As an eventual supplement to our existing linear photodiode array system, imaging plates will allow us to measure a large enough 2- θ range for quantitative x-ray analysis and, with the use of a Soller slit assembly, will allow us to map the weld HAZ in a more efficient row-by-row manner than the point-by-point manner we currently use.

A new experimental setup was designed to incorporate an inert gas enclosure around the SRXRD welding experiment to minimize oxygen contamination of the weld during future experiments. This enclosure is presently being fabricated at LLNL and will be ready for the next SSRL run in March 1996. During this run we plan to (1) completely map the phases that exist in the weld HAZ of grade 2 titanium, (2) perform a simple Soller slit experiment with an imaging plate detector, and (3) provide SRXRD analysis of the kinetics of Cu-Al₂ θ -phase dissolution in aluminum-copper alloys as part of a collaboration with the University of Alabama at Birmingham.

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Molecular Level Study of Shock Propagation in Damaged Triaminotrinitrobenzene

Laurence E. Fried and Craig Tarver

Science-based stockpile stewardship requires the national laboratories to examine in greater detail the basic physical problems underlying the safety of the nuclear stockpile. One such problem is high-explosive sensitivity. It is well known that most explosives become more sensitive when defects are introduced through heating or mechanical work. In this report, we examine how shock velocities and temperatures are different in pure and porous triaminotrinitrobenzene (TATB) crystals. Our ultimate goal is to determine a scientifically based model of high-explosive (HE) sensitization as a function of crystal defect concentration.

Over the past decade, molecular dynamics simulations have been applied to shocks in a range of materials.¹⁻⁵ There have been few applications, however, to typical energetic materials. Energetic materials used in military applications are typically large molecules containing several nitro groups, e.g., trinitrotoluene (TNT) and TATB. Many common energetic materials have over 20 atoms.

The shock dynamics of large floppy molecules is expected to be different from the shock dynamics of diatomics and triatomics. One simple difference is found in the large number of vibrational modes. TATB, for example, has 66 vibrations. At the shock front, however, all energy is channeled into translations. This leads to a huge translational temperature overshoot at the shock front. For detonation shocks this overshoot can be as large as 20,000 K.⁶

In the present report, we will simulate shocks in nonreacting TATB. TATB has a shock-initiation threshold of 3 km/s or above, depending on its preparation and porosity. We will study the propagation of shocks with particle velocities of 1 km/s for 10 ps. Given the shock-initiation threshold of TATB, we expect that there will not be significant chemical reaction during the time span of the simulations, thus justifying the use of nonreactive potential surfaces.

Simulation Method

All the atoms of TATB were included in the simulation. The intramolecular forces included harmonic bond stretching, a $\cos(\theta)^2$ bend interaction, and a $\cos(\phi)$ torsional interaction. The functional forms and parameters were taken from the DREIDING⁷ molecular mechanics potential energy surface. Lennard-Jones interactions were used for the intermolecular forces. Periodic boundary conditions were enforced transverse to the shock front. Free boundary conditions were employed in the direction of the shock front.

We simulated two-dimensional (2-D) TATB crystals. The crystal structure of TATB consists of overlapping planes of molecules. In the simulation, the TATB molecules were arranged in a hexagonal lattice. Porous TATB samples were achieved by randomly removing molecules with a given probability. This is a simplified model of a unimolecular decomposition process, where the TATB has decomposed into products small enough to diffuse out of the crystal lattice.

Results

We investigated the shock structure of perfect crystals of TATB first. We found it sufficient to use a TATB crystal with 10 lattice spacings in the transverse (y) direction and 40 lattice spacings in the shock (x) direction. The shock velocity achieves a steady state after 1 ps.

We next considered the propagation of shocks in porous TATB. In these simulations, molecules were randomly removed from the 2-D lattice with a specified probability. The particle velocity in these simulations was 1 mm/ μ s. Figure 1 shows a snapshot of a 10-ps simulation. A simulation cell of 75 (x) by 19 (y) nm was used. The shock front is spread out over roughly 10 nm. The collapse of voids leads to the production

of hot spots and a highly nonuniform temperature distribution behind the shock front. Similar effects are seen in 40% porous TATB. A 75- × 75-nm simulation cell was used in this case to obtain better averaging over the many pore sizes. Figure 2 shows a snapshot taken at 10 ps. The shock speed is much lower in the highly porous material. The shock front is very broad in both the 20% and 40% porous material, in comparison with the shock front widths of a few lattice spacings seen in molecular dynamics of pure materials.²⁻⁴ Equilibration of the system into a well-defined shock front and steady-state zone behind the front has not yet occurred.

It is interesting to compare the effect that porosity has on shock temperatures. The increased temperatures caused by void compression (referred to as hot spots in the explosives literature) lead to high average temperatures in the porous material. Figure 3 shows shock temperatures for 20% porous and 40% porous TATB taken at a time of 10 ps. The increase in temperature with porosity is a well known effect.⁸ Porosity increases the average temperature behind the shock front by nearly a factor of 2.

The break in slope in the 20% porosity temperature distribution shows that equilibration to a steady shock front has begun within the 10-ps simulation time. There is no such break in the 40% porosity distribution, indicating that equilibration times are much longer than 10 ps.

There is a broad distribution of particle velocity accompanying the temperature distribution in the porous materials. Figure 4 shows the particle velocity as a function of position for 20 and 40% porous TATB.

Discussion

In this report we have described how shock properties of two-dimensional TATB crystals change as a function of random porosity. The most dramatic effects seen are a factor of 4 decrease in the shock velocity and a factor of 10 or more increase in the shock equilibration time. Temperatures behind the shock front increased by roughly a factor of 2.

To date, we have established how temperatures are significantly higher in degraded porous TATB than in a pure TATB crystal. The next step is to link temperature to the underlying reactivity of the HE, thus leading to a predictive theory of how porosity affects HE sensitivity.

Figure 1. A simulation of 20% porous TATB is shown at time of (a) 0 ps, (b) 2.5 ps, and (c) 5 ps. The molecules are shaded according to their kinetic energy; pure white corresponds to 800 K.

Figure 2. A simulation of 40% porous TATB is shown at a time of 10 ps. The molecules are shaded as in Figure 1.

Figure 3. The temperature profile across the shock front is shown for simulations of 20% and 40% porous TATB. The calculated shock temperature of pure TATB is shown for reference. Distance is shown in units of one lattice spacing.

Figure 4. The average particle velocity across the shock front is shown as a function of distance for 20% porous and 40% porous TATB.

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Deformation Mechanisms in U-6Nb

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We are studying the U-6Nb alloy to establish the deformation mechanisms that occur during mechanical strain. This information is needed to better understand formability behavior of the alloy at large strains and the response of applied forces on components fabricated from this alloy. The approaches being used are in situ straining of the alloy in the transmission electron microscope and large-strain deformation experiments using mechanical testing. Results in the literature and those obtained in this study suggest that more than one mechanism may be operative.

Microstructural Examination of U-6Nb

During this research period, microstructural studies by transmission electron microscopy (TEM) and electron diffraction (ED) have been focused on in situ straining within the transmission electron microscope. The need for in situ straining came about from the difficulty in distinguishing individual dislocations within the complex microstructure as part of the overall investigation of the deformation mechanisms in U-6Nb alloys. Figure 1 is a bright-field image showing an extremely high density of twins in a specimen that was strained to approximately 50% in torsion. It is not readily apparent that dislocations or dislocation clusters exist; tilting experiments aimed at

Figure 1. Bright-field image from a highly strained U-6Nb specimen revealing a high density of twins.

improving the dislocation contrast proved unsuccessful. For these reasons, in situ straining was attempted in the TEM.

The geometry of the in situ tensile specimens is that of a thin plate: 7.5 mm long, 2.7 mm wide, and 0.12 mm thick (Figure 2). The specimen has two small holes machined along the centerline in which pins are used in conjunction with clamps to fix the specimen to the straining holder. While being recorded on video, the specimen is strained by pulling uniaxially on the specimen. Conventional electropolishing techniques are used to thin the center of the specimen to electron transparency.

U-6Nb is a shape-memory alloy suggesting, in principle, that the alloy should first deform elastically similar to most other materials. The ideal stress-strain curve should then demonstrate a flattening in which plastic strain by the motion of twin boundaries and the migration of variant boundaries is the expected deformation mechanism. Upon further straining, after the specimen is fully detwinned, plastic deformation

Figure 2. Schematic diagram of in situ TEM specimen geometry.

is anticipated to progress by more conventional mechanisms, such as dislocation motion. The torsion stress-strain curves in our alloys do not show a distinct flattening but rather a subtle change in slope, indicating a shorter region of twin boundary motion.

Preliminary results from the in situ straining are in line with this mechanical testing observation. Deformation is observed to occur by the motion of dislocations (Figures 3 and 4) taken from the in situ video. The bands running diagonally from the upper left to the lower center are the traces of the dislocations that have passed through the specimen from the hole (at the top) toward the thicker regions.

Figure 3 illustrates the microstructure at one stage during the experiment. Deformation bands appeared to be generated at the specimen hole and progressed into the thicker regions of the foil, initially starting relatively far to the left of this image and progressing to this point.

Figure 4 was extracted from the video approximately 1 s later. Within that time period, a number of dislocations crossed the specimen from the upper right to the lower left of the image, resulting in the dark contrast band. These preliminary results from the in situ straining are quite encouraging but are still limited by the difficulty of specimen preparation. Presently, these experiments cannot be interpreted quantitatively because the exact stress state of the specimen is unknown; however, the qualitative observations at various strain levels should prove beneficial in determining the mechanisms of deformation. Additional in situ straining experiments are

forthcoming to focus on different regions of the stress-strain curve.

Mechanical Testing of U-6Nb

We continued our study of mechanical testing methods appropriate for studying U-6Nb. Previously, we had focused on thick-walled torsion specimens to obtain somewhat "uniform" strain as achieved in thin-walled tubes and to avoid buckling as achieved with solid rods. The solution used for the thick-walled cylinder available was based on a number of approximations and given by Eq. (1):

$$\tau = \frac{(3 + n^* + m^*)M}{2\pi r_s^3} \left[1 - \left(\frac{r_i}{r_s} \right)^{3 + n^* + m^*} \right]^{-1}, \quad (1)$$

where τ is the shear stress; n^* is the strain-hardening exponent; m^* is the strain-rate sensitive; M is the torque; r_s is the surface radius; and r_i is the inner radius.

The shortcoming of this approach is that the equation is not an exact solution. Recently, we have been using an integration method proposed by G. Canova that can provide accurate solutions to these questions, although n^* and m^* will need to be determined. Our first calculations are shown in Figure 5 for a solid specimen, in comparison to the Fields-Backofen method. We are in the process of looking at this for thick-walled specimen.

Figure 3. Bright-field image taken from the in situ experiment revealing dislocation traces running from upper left to lower center.

Figure 4. Bright-field image from the in situ experiment about 1 s after Figure 3. A series of dislocations have passed through the image from the upper right to the lower center leaving the dark contrast line.

Figure 6 shows a tensile stress-strain curve for U-6Nb. It is interesting to note that the torsion and tensile test results differ significantly. One possibility is that hydrostatic stress components exist in tensile but not in torsion. These hydrostatic stress components may cause a phase transformation or modify the observed transformation. Compression tests may verify whether the "unevenness" in the tensile tests can be shown to be dependent on hydrostatic stress components.

Figure 5. Shear stress-shear strain curves obtained by reducing the torque angle of twist data using two methods. The reasonable agreement between the two methods for solid specimens is desirable for solid specimens, indicating the integration method is valid, which will be applied to thick-walled torsion specimens.

Figure 6. Tensile stress-strain curve for U-6Nb. Besides showing the "double knee" (at ~0.04 strain) due to the shape memory effect, a possible change in deformation mechanisms may occur at strains of 0.13. The difference between torsion and tension is not well understood.

Aerogel Sensor Development

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Our objective is to determine the feasibility of using doped aerogel materials as combination desiccants and detectors for sorbed gases. Passive sorption media are useful within weapon enclosures to take up and hold moisture and other contaminants, and completely passive sensors (i.e., containing no electrical connections) are desirable for in situ diagnostics in weapons and weapon-storage containers. This is a development effort for such a passive device,

consisting only of quartz fiber light guides and aerogel material, that would serve a dual-purpose function as a desiccant and a detector for moisture and off-gas contaminants within enclosures. If feasible, the aerogel sensors could be used as passive, in situ monitors within weapons or storage containers.

Aerogels are lightweight, open-porosity materials that have a huge internal surface area (> 0.2 acres per gram of material is typical). It is known that if they

are predried, aerogels will preferentially "pump" polar gases such as water from other atmospheres. Moreover, the large surface area of aerogels provides a large sorption capacity per gram of material, and polar molecules are retained by the aerogel until relatively high temperatures are reached. Prior work has determined that (1) silica aerogel is useful over a temperature range of 4 to 600 K, (2) organics that were trapped in the aerogel were not released up to a temperature of 420 K, and (3) the silica aerogel has remarkable radiation resistance (surviving up to 100 Mrad).

It is also possible to dope the aerogel with compounds that would react or interact with contaminant molecules, resulting in colorimetric or photometric changes to indicate the presence and possibly the amount of the contaminant. For example, in previous work we have successfully doped silica aerogels with a variety of fluorescent dyes such as fluorescein, rhodamine, and chloro-aluminum-phthalocyanine. The resulting aerogels are transparent and colored, and they strongly fluoresce when exposed to ultraviolet light. Our data suggest that the aerogels are heterogeneous and that the dye molecules are trapped within the aerogel pores rather than bonded within the silica skeleton. If this is the case, we would expect the fluorescence spectrum of the dye molecules to be affected by the presence of other sorbed species and that they could be detected by means of the spectral change. In another example, we synthesized an aluminosilicate aerogel that exhibits phosphorescence; we expect that the decay time is strongly affected by the presence of sorbed molecules and thus could be a means for detecting them. Alternatively, the aerogel can be doped with compounds that give a color change upon sorption. We believe that we can construct a simple passive detector consisting only of the doped aerogel and an optical fiber used to spectroscopically probe it within an enclosure.

Technical Progress

In FY 1995, we determined if shifts in the spectrum of a fluorescent dye doped silica aerogel were correlated with sorption of selected test species. We found no measurable response; however, we identified two candidate spectroscopic effects in high-surface-area aerogels, which can be used to detect moisture: the decay rate of photoluminescence in aluminosilicate aerogels and the spectral change in vanadium-doped silica aerogel, due to absorbed moisture. Both effects were evaluated as analytical detectors; the colorimetric effect was more sensitive than the time decay. We focused our efforts to develop this method. We then did a systematic study to

determine the range of analytical utility of the vanadium-doped aerogel.

Stiegman showed that silica sol-gels doped with less than 1 mol% of vanadium change color upon exposure to moisture and other gases.¹ We made vanadium-doped silica aerogels and confirm that there is also a color change in them associated with moisture absorption. Stiegman proposed that the water reacts with the vanadium sites to cause coordination changes from tetrahedral to octahedral, resulting in color changes from green to red. We measured the spectral shift of the vanadium-doped silica aerogel vs moisture loading. Figure 1 shows how the transmission spectrum changes for an aerogel doped with about 2 wt% vanadium, when it is exposed to various concentrations of moisture. These data were taken using a Perkin Elmer Model 800 UV-VIS Spectrometer while the aerogel sample was exposed to moisture at a fixed relative humidity. The spectral signature shifts to longer wavelengths as the water is absorbed. It is noted that the transmission change is greatest at about 540 nm for the low water concentrations, but it saturates and becomes greatest again at about 850 nm for the higher concentrations. This result suggests that a wide range of sensitive detection can be obtained by using at least two separate wavelengths with the doped aerogel sensor.

Our measurements confirmed that moisture can be detected quantitatively with vanadium-doped silica aerogel and that the method can be analytical if properly calibrated. We estimated the sensitivity and detectability range from our measurements. This

Figure 1. Plot showing the spectral shift of vanadium-doped silica aerogel as water is absorbed into it: O is dry, □ is 0.37 mmol, ◇ is 0.74 mmol, × is 1.04 mmol, and + is 1.3 mmol of water.

detector should detect as little as 10 ppm water in air and should have a detectability range from 0 to 10 mmol for each gram of aerogel material used. Thus, vanadium-doped aerogel is promising as an in situ detector for moisture using fiber optics to readout.

We also tested the capability of aerogels for sorption of water vapor. The sorption behavior and performance of the aerogels were examined and compared with other common desiccants. We measured sorption rates, capacities, and retention times vs temperatures for silica aerogels and vanadium-doped silica aerogels.

We measured the sorption of moisture on selected samples by exposing them to 100% relative humidity and monitoring the weight gain as a function of time. Figure 2 shows the results for silica aerogel and a common desiccant, silica gel. We determined that the capacity of the aerogel to absorb water is inversely proportional to its density. We also found that the low-density (high-porosity) aerogel can absorb nearly twice its weight in water.

We determined that there are three distinctive absorption behaviors in predried aerogels, and we propose the following: The first moisture to enter the aerogel chemisorbs (i.e., hydrogen bonds) to the silica surface; the next moisture forms transition layers; and the remainder of the moisture physisorbs to the silica surface. These three distinct regions are identifiable on the curve for silica aerogel in Figure 2: a rapid linear absorption up to about 10 wt%, a transition

Figure 2. Plot showing the absorption of water vs time, comparing the desiccant properties of silica aerogel vs silica gel exposed to 100% relative humidity. The silica gel saturates at about 30% weight gain, whereas the aerogel continues to absorb and saturates at nearly 200% weight gain.

region to about 30 wt%, and a nearly linear absorption up to 60 wt% and beyond. During the latter stage, the silica aerogel shrinks irreversibly. We speculate that the moisture condenses (by capillary condensation) within the aerogel, causing the shrinkage. The very low density aerogel undergoes a volume change by a factor of about 80 during this phase. The vanadium doped silica aerogel exhibits the same behavior as the silica aerogel. We found that the doped aerogel absorbs up to 30% of its weight in moisture, which is detectable as a color change, but the additional water absorption does not cause further detectable color change.

We also exposed small aerogel spheres (about 1 to 3 mm diam) to moisture-laden air (about 24% relative humidity) and monitored the weight gain using a microbalance in a Mettler Model 119 Thermogravimetric Analyzer. The results are similar to the absorption behavior described above, i.e., the aerogel rapidly absorbs the moisture and saturates. The absorption rate determined from these measurements is about 0.1 g H₂O / g aerogel / min. These measurements were also made at elevated temperatures, and we determined that the aerogel absorbs greater than 50% of its room-temperature capacity at 80°C. Clearly, all of the aerogels exhibit exceptional desiccant performance.

Future Work

In FY 1996, we will construct a prototype aerogel detector and demonstrate proof-of-principle for real-time, in situ monitoring. We will set up a bench-scale model simulating a weapon environment and perform measurements using prepared moisture concentrations. Additional work will be needed to qualify this method for actual implementation in weapons and storage containers.

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Mechanism of Ductile Rupture in the Aluminum–Sapphire System Elucidated Using X-Ray Tomographic Microscopy

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The fracture of a thin metal foil constrained between alumina or sapphire blocks has been studied by a number of investigators. The systems that have been investigated include aluminum,^{1,2} gold,³ niobium,⁴ and copper.⁵ Except for Al–Al₂O₃ interfaces, these systems exhibit a common fracture mechanism: Pores form at the metal–ceramic interface several foil thicknesses ahead of the crack that, under increasing load, grow and link with the initial crack. This mechanism leaves metal on one side of the fracture surface and clean ceramic on the other. This has not been the observation in Al–Al₂O₃ bonds where at appropriate thicknesses of aluminum, the fracture appears to proceed as a ductile rupture through the metal.

The failure of sandwich geometry samples has been considered in several published models.^{6,7} The predictions of these models depend on the micromechanic mechanism of crack extension. For example, Varias et al. proposed four possible fracture mechanisms: (1) near-tip void growth at second phase particles or interfacial pores and coalescence with the main crack, (2) high-triaxiality cavitation, i.e., nucleation and rapid void growth at highly stressed sites at distances of several layer thicknesses from the crack tip, (3) interfacial debonding at the site of highest normal interfacial traction, and (4) cleavage fracture of the ceramic. Competition among the operative mechanisms determines which path will be favored.

This paper addresses the question of why the fracture of the Al–Al₂O₃ system appears to be different from other systems by probing the fracture mechanism using x-ray tomographic microscopy (XTM). We have experimentally duplicated the simplified geometry of the micromechanics models

and subjected the specimens to a well-defined stress state in bending. The bend tests were interrupted and XTM was performed to reveal the mechanism of crack extension.

Experiment

The system of pure aluminum bonded to sapphire exhibits low x-ray absorption, chemical compatibility, and a tendency to rupture in a ductile manner. Sapphire avoids the problems associated with grain pull-out and porosity present in polycrystalline alumina. The sapphire was purchased as cylinders 16 mm in diameter × 20 mm high with faces polished parallel to (0001) ±1 deg and 1/10 ($\lambda \approx 550$ nm) flatness. The aluminum foil purchased was 99.999% pure and 50 μ m thick. The foil was laser-cut into disks 19 mm in diameter. A support ring assembly made of commercially pure aluminum was attached to the perimeter of the disk by laser welding. Because bonding of the aluminum foil between two cylinders was to be accomplished by ultrahigh vacuum (UHV) diffusion bonding,⁸ the support ring facilitated the remote handling of the disks inside the diffusion bonding machine. Otherwise, the materials were used in the as-received state.

The surfaces of the sapphire to be bonded and both sides of the aluminum foil were sputter cleaned with 1 keV Xe⁺ impinging at 15 deg above the horizontal. Specimens were rotated during sputtering. The surface elemental composition was characterized using Auger electron spectroscopy. All surface contaminants thus measured, including the oxide layer on the metal, were removed to below the detection limit of the technique. Previous experience with aluminum shows that many hours of exposure are necessary to reform a contamination layer in the UHV environment (<10⁻¹⁰ Torr). The specimens were

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stacked and a load of 10 MPa applied. The specimens were heated to 600°C and held for 38 h. Relatively long bonding times were required because of variations in the thickness of the aluminum foil, which requires creep to bring the surfaces into contact and eliminate all void space.

Bend beams were cut from the diffusion bonds using diamond cutting. The beams had nominal dimensions of $3 \times 3 \times 40$ mm. To ensure that failure initiated in the metal foil rather than at a flaw in the ceramic, a thin notch was placed within the metal. The notch root diameter was 40 μm , and the notch was 500 μm deep. The beams were loaded in four-point loading with an inner span of 10 mm and outer span of 30 mm. Several beams were loaded to failure to characterize failure stresses.

Specimens examined with XTM were first characterized in the as-notched condition. The beam was then loaded until the first sign of nonlinearity in the load vs crosshead displacement plot was observed. The mechanical test was interrupted, the specimen removed, and an XTM scan performed. The mechanical test was subsequently resumed to strain the beam further. This iterative sequence was continued for as long as was practical.

Ductile metals are opaque to the wavelengths of visible light. Hence, observations of the mechanisms of crack extension have not been possible in these materials. The advent of synchrotron-based XTM⁹ has made it possible to determine the three-dimensional variations in density of specimens several millimeters in dimension for low-atomic-number materials at resolutions approaching 1 μm .

In performing the XTM scans, the x rays from a synchrotron source (the eight-pole wiggler beamline 4-2 at the Stanford Synchrotron Radiation Laboratory) were passed through a Si(220) monochromator to select 25-keV photons. After passing through the specimen, the x rays struck a CdWO_4 scintillator. The light emitted from the scintillator passed through magnifying optics and was collected by a charge-coupled device (CCD) camera at a magnification sufficient to give the volume elements (voxels) in the reconstructed image the size 5.3 μm on a side.

Radiographs were collected at 0.5-deg increments of sample rotation over a range of 180 deg. Reference images of the unobstructed x-ray beam were acquired every 3 deg to correct the radiographs for beam inhomogeneities, beam instabilities, and pixel-to-pixel gain variations in the CCD array. A three-dimensional image, which represents the product of the pixel size and the absorption coefficient, was reconstructed as

slices delineated by the rows of the CCD array using a filtered backprojection algorithm.

Defects in the scintillator can give rise to bright or dark spots in radiographs that are not compensated for through normalization to the reference image. Such spots result in the appearance of bright or dark (usually dark) "rings" in the reconstructed slice. Most rings were removed using an interpolation algorithm on experimental sinograms. However, some rings remained that can, in severe cases, give rise to contrast resembling voids, i.e., relatively low values of the absorption coefficient-thickness product. Such severe rings were found in the scans of the as-prepared sample and after the first deformation.

Locations of interfaces are delineated by pairs of bright and dark fringes in the XTM contrast. Although the origin of these fringes is currently not fully understood, the point of contrast reversal has been empirically shown to mark the interfaces. Voids, which have relatively low value of the absorption coefficient-thickness product compared with the sapphire or aluminum are readily revealed by XTM. Voids exceeding 2 voxels in volume were identified and counted with an efficient, single-pass cluster labeling algorithm developed by Hoshen and Kopelman¹⁰ and described in more detail elsewhere.¹¹ All void contrasts, including those from ring artifacts, are displayed in Figure 1. Although it is possible to follow the growth of isolated voids, this was not done in this initial study.

Results

As-Prepared Sample

XTM revealed that the sample prepared in the four-point bend geometry exhibited two dense interfaces between the aluminum and the sapphire. No resolvable voids were observed outside of three regions affected by ring defects. Figure 1(a) shows a rendering of the volume studied with XTM. The profile of the notch was extracted from this data and was used as input for finite element calculations to calculate the stress state of the sample.

First Deformation

Figure 2(a) shows the load-displacement curve for the first in a series of three deformations. Loading was relaxed at the first indication of the onset of plasticity. XTM revealed four resolvable (size greater than 2 voxels) voids located at the interfaces between the metal and the sapphire. These voids were between 3 and 7 voxels in volume. Three of the voids were

Figure 1. Rendering of (a) undeformed volume, (b) after first loading, (c) after second loading, and (d) after third loading. Voids appear as lighter contrast features in the volume.

lenticular in nature. The fourth, and largest, had an aspect ratio (ratio of the radius of gyration normal to the interface to that in the plane of the interface) of about 1; i.e., the largest void was spherical. Figure 1(b) shows the rendered volume with voids (including those resulting from ring artifacts and those 1 voxel in size). Finite element modeling results for the maximum in triaxiality, maximum in tensile traction at the interface, and their locations relative to the notch root are shown in Table 1.

Second Deformation

Figure 2(b) shows the load-displacement curve for the second deformation. XTM revealed 53 resolvable voids located at the interfaces between the metal and the sapphire. Figure 3 shows a slice through the volume, revealing several voids at the interfaces. A common feature of this is that they are all at the interfaces, and voids are never seen to nucleate on opposite sides of the foil directly across from each other; they are usually staggered with respect to each other. Voids less than about 30 voxels in size are usually lenticular in shape. Between volumes of 30 to 100 voxels, the aspect ratio grows to about 0.6. For volumes in excess of 100 voxels, the aspect ratio decreases to about 0.2. Figure 1(c) shows a rendering of the void distribution and illustrates the increase in the void population compared with the first deformation.

Third Deformation

Figure 2(c) shows the load-displacement curve for the third deformation. XTM revealed 131 resolvable voids located at the interfaces between the metal and the sapphire. While some small voids do take on a spheroidal shape, the general trend for the smallest and the largest voids is to have aspect ratios of less than 0.2. Voids in the range of 200 to 900 voxels in volume tend to have aspect ratios approaching 0.4. The void population has dramatically increased and the voids have spread ahead of the notch (Figure 1[d]).

Table 1. Finite element modeling results for the maximum in triaxiality, maximum tensile stress at the interface, and their locations relative to the notch root relative to the foil thickness.^a

Loading	σ_m/σ_o	X_m/h	σ_{yy}/σ_o	X_{yy}/h
1	4.1	2.3	4.5	2.3
2	5.4	2.8	5.9	2.6

^a Yield stress used in this calculation was 12.2 Mpa, foil thickness was 50 μm , and notch depth was 630 μm .

Discussion

XTM has been used to elucidate the mechanism of ductile rupture of a 50- μm -thick aluminum foil bonded between two sapphire cylinders subjected to Mode I loading. At the onset of plasticity, small lenticular voids form at each interface at a location consistent with the maxima in triaxiality and tensile traction at the interface. As such, this work reveals that debonding plays an important role in the failure at the earliest stages of plasticity. Previous observations of rupture in this system revealed the presence of voiding on the fracture surfaces, e.g., see Refs. 1 and 2. However, the authors were only able to link the origin of some voids with the interfaces, i.e., the generalization of this observation to all voids was not clear.

In this investigation, all voids were initially associated with an interface. Further, using conventional fractography, the mechanism of void nucleation and growth could not be revealed. The lenticular nature of these voids as revealed by XTM suggests that they may be formed by debonding and propagation of an interface crack rather than by nucleation and growth via dislocation agglomeration. The existence of debonds at interfaces in aluminum is consistent with observations in other systems that debond but do not exhibit the extensive ductile dimpling found in aluminum, e.g., gold,³ niobium,⁴ and copper.⁵ The observations of this work suggest that the tendency of a system to rupture in a ductile or brittle fashion may be controlled by the interplay of the interface bond strength and the yield strength of

the metal. The formation of a void at an interface locally relaxes the constraint, thus eliminating the possibility that a void will nucleate directly across the foil on the opposing interface. This increases the constraint nearby, giving rise to the tendency of the voids to be staggered with respect to each other.

As deformation proceeds, voids of intermediate size tend to become spherical under the influence of the triaxial stress state, which serves to relieve the constraint locally. It is reasonable to conclude that the maximum in the constraint then shifts to locations farther in advance of the notch root where more small debonds form. At high strains, spherical voids continue to grow until they interpenetrate, which eventually leads to the formation of the ductile ligaments observed in fractographs. There appears to be a second class of voids that remain lenticular throughout the deformation. These seem to be lenticular voids that have grown past some perhaps critical size above which the tendency to become spherical is diminished.

Conclusions

UHV diffusion bonding has been used to make model specimens in the aluminum-sapphire system. The micromechanics of failure for this system were observed using XTM. The primary findings are that (1) damage ahead of the notch initiates by interface debonding at a location coinciding with maxima in triaxiality and tensile traction at the interface; (2) debonding occurs at the most early stages in the observation of plasticity; (3) the debond expands for a

Figure 2. Load as a function of crosshead displacement for (a) first loading, (b) second loading, and (c) third loading.

Figure 3. Slice through volume perpendicular to notch after second deformation showing voids on both interfaces.

limited distance, likely arresting because of crack tip blunting; (4) this lenticular debond then becomes spherical with further strain; and (5) intergrowth of the spherical voids leads to the typical ductile rupture fracture surfaces observed in this system. Future efforts to model this effect will need to include the debonds at the interface that alter the state of stress.

Acknowledgments

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Attribution Technology Program

Ron Lougheed

Our activities in FY 1995 were focused in two areas: (1) the study of Comprehensive Test Ban (CTB) evasion scenarios (post-explosion attribution) and (2) the attribution assessment of illicit nuclear materials (pre-explosion attribution). In the first area, our activities were primarily technical; in the second area, our activities were primarily in program development.

One of the most likely locations a CTB evader might choose for detonating a nuclear device is the open ocean. Use of the open ocean provides the opportunity to hide the radionuclide signatures from a nuclear explosion and, even if the radionuclide signatures were detected, to escape attribution. A previous incident is a possible model for this scenario. With collaborators in the Regional Atmospheric Sciences Division, we performed a study of various ocean scenarios that a CTB evader might use to hide a nuclear test. By modifying one of the best available fallout models, we developed a new model to calculate the concentration of explosion debris that would remain in the ocean at the site of the explosion. This model includes the effects of a local rain storm on the fallout. We calculated the resulting gamma radiation from the radioactive ocean slurry and deduced the time window in which it could be detected by an aerial survey. We found that for many scenarios of interest, the ocean slurry could be detected for many days, even weeks, and that radiochemical analysis of samples of the slurry could provide valuable clues for attribution.

We continued our activities in the pre-explosion attribution assessment of special nuclear materials (SNM) using radiochemical methods. Our work has shown that by measuring isotopics and composition of minor components in the SNM in addition to the isotopic composition of the SNM, much information about the production and history of the material can be obtained. In the case of plutonium, for example, the type of reactor used to produce the material, length of irradiation, reprocessing technique, enrichment of the uranium, time of chemical separations and casting as a metal, and even evidence of other operations in the plant can be revealed.

We developed a collaboration of technical experts in radiochemical analysis from LLNL, Pacific Northwest Laboratory (PNL), Los Alamos National Laboratory (LANL), SRTC, and Oak Ridge National Laboratory (ORNL). The collaborators developed a joint proposal for an interlaboratory network to perform attribution assessment of interdicted illicit nuclear materials.

We wrote a white paper with PNL collaborators on the concepts and issues of attribution assessment of illicit nuclear materials. This report became the basis for an interagency report on the subject, which was in turn the basis for a presidential directive giving DOE significant responsibility in this area.

We hosted a Nuclear Forensic Tools Workshop at LLNL. Technical experts in radiochemical analysis from LLNL, PNL, LANL, SRTC, and ORNL participated in the workshop. We identified and prioritized the experimental tools that are expected to be of value in the analysis of illicit nuclear materials.

LLNL hosted the International Conference on Nuclear Smuggling Forensic Analysis. The participants included technical experts and government representatives from Canada, France, Italy, Germany, Japan, the United Kingdom, the United States, EURATOM, the Czech Republic, Estonia, Ukraine, Bulgaria, and Poland. The U.S. Government participants included the DOE, FBI, NPC, State Department, Customs, Air Force, and DOE national laboratories. This highly successful conference led to the development of an ad hoc Technical Working Group, which will meet in early 1996 to design an international exercise. The exercise is likely to involve the analysis of actual illicit nuclear materials.

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Special Nuclear Materials Detection and Materials Control

Ron Loughheed

Our research activities in FY 1995 focused on the detection of Special Nuclear Materials (SNM) by developing and demonstrating the use of advanced gamma detection methods. We conducted experiments to demonstrate the feasibility of isotopic analysis of plutonium under water using a LLNL-developed cryocooled germanium detector to measure and analyze the plutonium gamma rays. Comparison spectra were taken with a conventional liquid-nitrogen-cooled detector. Spectra of standards were taken for later comparison in field experiments. Monte Carlo simulations of the detector response were also performed to understand the results. Additional work will help determine the design criteria for more sensitive detectors. This work could be applied to search missions for radioactive materials.

In FY 1995, we completed a proof-of-principle that one can obtain the radial position(s) of energy deposited by a gamma ray in a conventional cylindrical germanium detector by analyzing the leading edge of the signal. We developed and tested an algorithm for performing this analysis rapidly and automatically. This work exercises the specialized high-bandwidth signal processing expertise developed under the test program. This effort could lead to enhanced capabilities for conventional detectors, such as the ability to suppress Compton events without an anticoincidence detector. It could also lead to enhanced capabilities for sophisticated detector arrays used for fundamental studies in nuclear reactions. A record of invention is in progress.

Beryllium Fuel Capsules for the National Ignition Facility

D. M. Makowiecki, C. S. Alford, and R. J. Wallace

Fuel capsule designs involving ablator materials other than the hydrocarbon polymers (CH) currently used in inertial confinement fusion (ICF) targets on the Nova laser may offer improved implosion performance in experiments being planned for the National Ignition Facility (NIF). The most interesting new ablator materials are boron and beryllium and certain compounds of these elements. Current capsule designs require a few percent of high-Z atoms in the CH ablator material for preheat and opacity control. A proposed beryllium capsule design uses an

alloy layer with a graded doping of copper. A few atomic percent oxygen or nitrogen in the ablator material is acceptable.

Beryllium or boron fuel capsules have to meet demanding requirements with respect to surface finish, sphericity, microstructure, and composition to be used as targets in ICF experiments. Complex processes for fueling the capsules involving fill tubes or plug and patch techniques would have to be developed if they are not compatible with the gas diffusion techniques currently used on polymer

capsules. A practical consideration affecting the use of beryllium or boron as ablator materials would involve a comparison of the potential benefits and the increased costs and complexity of fabricating and fielding the new fuel capsule design.

We have made significant technical advances over the past few years in the deposition of complex beryllium and boron films by magnetron sputtering. The need for high-quality x-ray optics fostered the development of sputtering techniques for depositing complex beryllium multilayer coatings with discrete and compositionally graded interfaces.¹ We have a unique capability for depositing high-quality boron films because of our exclusive use of high-purity and fully dense boron sputtering targets.² In addition, we developed processes for uniformly depositing these low-Z materials on microspherical mandrels and powders with micrometer-size particles and have a facility for the safe deposition and handling of beryllium coatings. This combination of technical capabilities, experience, and facilities made the development of a sputtering process for fabricating beryllium fuel capsules a reasonable goal. We proposed to accomplish this goal by modifying a similar process used by Chen and Alford³ to fabricate smaller beryllium capsules for early ICF experiments. We report the experiments that resulted in the fabrication of high-quality beryllium capsules in the first six months of this project.

Experimental Methods

The beryllium films were prepared in a small vacuum coating chamber mounted inside a chemical fume hood with a HEPA-filtered exhaust. A liquid helium cryopump produced a base pressure of less than 2.6×10^{-6} Pa in the system prior to all coating experiments. Argon sputter gas was distilled directly from a liquid reservoir. The argon pressure was maintained at a fixed value in the experiments by mechanically restricting the pumping speed and controlling the gas flow rate. Three small magnetron sputtering sources in a triangular array were vertically positioned about 6.3 cm above the substrate pan (Figure 1). The dish-shaped pan could be configured for coating either flat substrates or microspherical mandrels. A piezoelectric crystal isolating the pan enabled the application of both a high-frequency oscillation for bouncing the microspheres and a negative voltage for bias sputtering. The coating process was monitored remotely by a video camera mounted on a viewport. The 3.3-cm-diam targets were machined from a beryllium rod with a maximum oxide content below 0.3 at.%. Copper wires

were brazed into modified beryllium targets for the deposition of alloy coatings. The substrates coated in these experiments included silicon wafers and both solid and hollow polystyrene spheres.

The process parameters selected for these initial experiments were developed for the deposition of beryllium optical coatings. An argon gas pressure of 0.4 Pa and a flow rate of 32 sccm was used in all sputtering experiments. The deposition rate on flat substrates for a single planar magnetron source operating at 175 W with beryllium and beryllium-copper composite targets was 0.99 and 1.05 nm/s, respectively. Composition of the alloy coating on flat substrates was determined qualitatively using Auger electron spectroscopy (AES). Based on this analysis, the composite target used in the capsule coating experiments had six copper wires 1.32 mm in diameter brazed into the center of the erosion ring.

Capsules were coated by operating two sources with pure beryllium and one source with the composite target. Prior to coating, the surface of the targets were sputter-cleaned against a shutter protecting the capsules. The sources were gradually brought to full power of 175 W dc to prevent temperature-related distortions in the polystyrene mandrels. At the same time, the amplitude and frequency of the signal to the piezoelectric oscillator was adjusted to produce a controlled random bouncing motion in the capsules.

Sphericity and surface finish of the capsules were measured using radial atomic force microscopy (AFM). Thickness of the beryllium coating, was measured using optical metallography and scanning

Figure 1. Three magnetron sputter source array positioned above the substrate pan containing the microspheres.

electron microscopy (SEM) of fracture surfaces. Surface morphology and microstructure were characterized by SEM and transmission electron microscopy (TEM). We measured the composition of the copper dopant in the beryllium coating using an electron microprobe of a polished cross section of the capsules.

Results and Discussions

Table 1 contains information on the sputtering process for coating microspherical mandrels with beryllium. The beryllium coating is thicker in experiment #32 because the targets in the sources were replaced and the process was repeated. Interrupting the coating process had only a minor effect on the microstructure of the beryllium coating (Figure 2).

In both experiments, the initial 40 mm of beryllium deposited on the polystyrene spheres was doped with copper. This was accomplished by sputtering the beryllium-copper composite target in one source at the same constant power of 175 W as the two sources with pure beryllium targets. The composition profile in Figure 3 was obtained by an electron microprobe analysis of a polished section of the beryllium coating in experiment #17. The change in composition resulted from the rapid erosion of the copper wires in the composite target. A specific composition profile

will be produced in future experiments by controlling the power on a homogeneous alloy target.

An AFM profilometer trace of the beryllium capsule from experiment #32 showed an unusual four mode or cubic structure (Figure 4). Recent experimental results indicate this is caused by the thermal distortions in the polystyrene shell and the sticking of capsules that occurs at the start of the coating process. The AFM data in Figure 5 show the smoothness and sphericity of the beryllium capsules. Table 1 shows a comparison of measured values on a beryllium capsule with the proposed NIF design criteria. Also, the results of some recent experiments indicate that the high-order roughness can be greatly reduced by bias sputtering.

Examination of the coating microstructure by SEM, TEM, and optical metallography reveal the unusual twisted microstructure shown in Figure 3 and trace amounts of porosity at the column boundaries. Similar microstructures have been observed in coatings deposited by multiple sputtering sources on rotating substrates. The impact of this unusual microstructure on capsule properties is unclear. However, the trace amounts of porosity at the column boundaries apparently give the beryllium capsules gas-diffusion properties similar to the uncoated polystyrene microshells. The potential benefit is the

Table 1. Magnetron sputtering process for fabricating beryllium capsules with a graded alloy layer.

Experiment	#17		#32		
Date	06/20/95		08/21/95		
Mandrel	Solid sphere		Hollow shell		
Material	Polystyrene		Polystyrene		
Diameter (mm)	~0.75		~0.5		
Wall thickness (μm)	—		~5.0		
Coating thickness (μm)	60.0		134.0		
Beryllium-copper layer (μm)	40.0		39.0		
Pure beryllium layer (μm)	20.0		95.0		
Deposition time (h)	17	15	15	20	35
Power (W dc)					
Source #1	175 ^a	0	175 ^a	0	175
Source #2	175	175	175	175	175
Source #3	175	175	175	175	175

^a Beryllium-copper composite target.

Figure 2. Scanning electron micrographs of a fractured beryllium capsule fabricated in experiment #32, as described in Table 1.

Figure 3. Change in the concentration of copper as measured by three electron microprobe traverses across the beryllium deposit from experiment #17, as described in Table 1. (a) Standard capsule (plasma polymer); (b) beryllium capsule.

possibility of filling the capsules by the current cryogenic gas-diffusion techniques that do not require fill-tubes or the use of drill and plug techniques. Changes in process parameters that affect the microstructure will also be evaluated for their effect on the gas-diffusion characteristics of the beryllium coating.

Conclusions

We demonstrated the potential of magnetron sputtering as a fabrication process for manufacturing beryllium fuel capsules for NIF. The application of process parameters developed earlier for the deposition of beryllium multilayer coatings for x-ray optics enabled us to fabricate capsules very similar to the

Figure 4. Comparison of radial AFM profilometer scans of a beryllium capsule and a typical plasma-deposited polystyrene capsule.

Figure 5. The measured power spectrum of a beryllium capsule.

Table 2. Comparison of a beryllium capsule and the proposed NIF criteria for ablator smoothness.

Modes	Beryllium capsule	NIF design
2-4	761	<1000
5-19	151	<300
11-30	26	<15
31-100	26	<20
101-1000	63	<10

preliminary design specifications. Recent experiments indicate that relatively minor changes to the sputtering process should result in significant improvements in both sphericity and surface roughness. Replacing the composite target with a copper-beryllium alloy target will provide us with the control needed to produce the required composition profile.

Magnetron sputtering has additional features that make it attractive as a fabrication process. The unexpected gas-diffusion characteristics of the sputtered beryllium capsules could facilitate their actual use in ICF experiments. Also, the batch-processing capability and the deposition rate of magnetron sputtering

should make it possible to fabricate large quantities of capsules at reasonable costs.

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Synthesis of 1,3,5-Triamino-2,4,6-trinitrobenzene and Other Insensitive Energetic Materials

Philip F. Pagoria, Alexander R. Mitchell, and Robert D. Schmidt

Vicarious nucleophilic substitution (VNS) of hydrogen is a well-established procedure for introducing carbon nucleophiles onto electrophilic aromatic rings.¹ The reaction involves the addition of a carbanion-bearing leaving group (X) to an electrophilic aromatic ring and subsequent rearomatization by loss of the leaving group through elimination as HX (Figure 1). This reaction has found application in the synthesis of a wide variety of nitroarenes and nitro-substituted heterocycles.²⁻⁴ Katritzky and Laurenzo⁵ extended this approach and reported the use of 4-amino-[1,2,4]-triazole (ATZ) as a VNS reagent to introduce amino groups onto nitro-substituted aromatic rings. Makosza and Bialecki⁶ subsequently reported the use of sulfenamides as VNS aminating reagents. They designed these reagents to be both good nucleophiles to easily add to the electrophilic aromatic ring and also possess a leaving group that forms a stable anionic species to be easily eliminated from the σ -adduct during rearomatization of the ring.

This approach prompted us to investigate the use of 1,1,1-trimethylhydrazinium iodide (TMHI)⁷ $[(CH_3)_3N^+-NH_2(I^-)]$ as a VNS reagent for the introduction of amino groups. We reasoned that TMHI would be sufficiently nucleophilic to substitute onto nitro-substituted aromatic rings, but it would be superior to the previous examples because the leaving group would be the neutral trimethylamine instead of a stabilized anionic species. In addition, there is a possibility that the hydrazinium halide would react with base to form the neutral ylide species $[(CH_3)_3N^+-NH^-]$, which may be the reactive species in the amination process. Indeed, when TMHI was reacted with various nitro-substituted aromatics, the amino functionality was introduced in good to excellent yields.

We found that the number of amino groups that may be added to the electrophilic aromatic ring is equal to the number of nitro groups present on the ring. This is the first example of the use of TMHI in a

Figure 1. Introduction of carbon nucleophiles by VNS.

VNS reaction and demonstrates an innovative approach to the synthesis of insensitive energetic materials. Previous methods for the synthesis of insensitive energetic materials generally relied on nitration of amino-substituted aromatic species or the reaction of chlorinated nitroaromatics with ammonia. Our VNS method allows amination of polynitro-substituted aromatics by the formal displacement of hydrogen, thus eliminating the need for chlorinated species. It also allows the synthesis of insensitive energetic materials not accessible by the previously described methods.

This chemistry led us to investigate the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 1,3-diamino-2,4,6-trinitrobenzene (DATB) from 2,4,6-trinitroaniline (picramide) using TMHI (Figure 2). Both TATB and DATB are insensitive energetic materials with total energy approximately equal to trinitrotoluene (TNT). TATB, however, is superior to TNT in metal acceleration experiments with 20% more kinetic energy. The synthesis involves the treatment of picramide at room temperature for 3 to 24 h with an appropriate amount of TMHI in dimethylsulfoxide in the presence of a two-fold excess of sodium methoxide (NaOMe). Quenching the reaction in aqueous acid gives TATB or DATB in 95% or 75%

yields, respectively. Preliminary results using ^{13}C -nmr spectroscopy show our material has fewer organic impurities than wet-aminated TATB.

Our new synthesis (Figure 2) is only a two-step reaction sequence starting from an inexpensive starting material, 4-nitroaniline, used extensively in commercial dye synthesis. It has many advantages over the current synthesis of TATB (Figure 3): (1) a significantly shorter two-step reaction sequence; (2) elimination of the problem of entrained ammonium chloride in TATB; (3) elimination of the expensive starting material and chlorinated aromatic species 1,3,5-trichlorobenzene, which is not currently available from domestic sources; and (4) it is performed at ambient temperature and pressure in contrast to the current procedure. This new method of synthesis may also lead to a significant decrease in the overall cost of TATB, which may facilitate expansion of industry use of TATB. A few of our industrial affiliates expressed interest in our synthesis in response to inquiries they had for the use of TATB in deep-hole oil explorations because of its extraordinary thermal stability. Most significantly, the VNS method should be more environmentally friendly than the current synthesis because it is a shorter synthetic sequence, many of the reagents and solvents may be

Figure 2. Synthesis of TATB and DATB using the VNS approach.

recycled, the aminating agent (TMHI) may be synthesized from surplus propellant, and the picramide starting material may be synthesized from the surplus munition ammonium picrate (Explosive D).

The use of TMHI as the aminating agent addresses a demilitarization problem currently being investigated in the United States. *uns*-Dimethylhydrazine $[(CH_3)_2N-NH_2]$ (UDMH) is a surplus propellant in the former Soviet Union currently being demilitarized by reduction to give ammonia and dimethylamine. TMHI is produced by the reaction of UDMH with methyl iodide in THF, providing an alternative demilitarization procedure for UDMH. TMHI is also synthesized directly from inexpensive hydrazine in 70 to 80% yield by alkylation with methyl iodide in the presence of aqueous base. This illustrates another advantage of our synthesis, namely that it may incorporate demilitarized explosives as feedstocks but is not solely reliant upon them.

We also investigated other VNS aminating reagents for the synthesis of TATB and DATB from picramide or 1,3,5-trinitrobenzene. The use of ATZ allowed the synthesis of TATB and DATB under conditions used for TMHI aminations.⁵ The use of methoxylamine hydrochloride gave exclusively DATB in 80% yield while the use of hydroxylamine yielded only 16% of DATB.

A study of product yields and distribution of various 3-substituted nitrobenzene derivatives was performed using TMHI (Figure 4). The results of our study were compared to the results using ATZ.⁵ ATZ was found to be regioselective, giving substitution

exclusively in the four-position relative to the nitro group, while TMHI showed no selectivity but presumably greater reactivity, giving all possible product isomers. There was a general tendency for TMHI to yield products in which the amine substitution occurs ortho- to the nitro group as the major components but there were exceptions. The superior reactivity of TMHI was also evidenced in the synthesis of TATB from picramide. Recent findings showed that TMHI goes to completion in less than 12 h, while the reaction with ATZ may take as long as 30 h to go to completion.

The synthesis of TATB by amination of 1,3,5-trinitrobenzene with TMHI suggested a mechanism in which each nitro group was available to stabilize a negative charge formed by reaction with the TMHI nucleophile, allowing the formation of an intermediate, trianionic species. This mechanism led us to investigate the amination of 3,5-dinitropyrazole (DNP), which carries an acidic hydrogen, to give ADNP. We reasoned that the acidic proton on DNP would initially react with one equivalent of base to form a stable nitronate anion leaving the second nitro group available to participate in the VNS amination. This would allow the synthesis of ADNP without needing a protecting group for the pyrazole proton. We found that the reaction of DNP with TMHI in the presence of excess potassium *tert*-butoxide gave ADNP in 70% yield (Figure 5). The structure of ADNP was confirmed by x-ray crystallographic analysis, isolated as a 1:1 complex with dimethylsulfoxide with a crystal density of 1.608 g/cm^3 .⁸

Figure 3. Current synthesis of TATB.

Summary

We introduced the use of TMHI as a VNS aminating reagent in the synthesis of amino-substituted nitroaromatics. We demonstrated a new synthesis of TATB and DATB from picramide using TMHI with significant advantages over the current method of synthesis. We have synthesized ADNP from DNP in one step using TMHI as the aminating agent.

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Uranium and Plutonium on Metal Surfaces

P. A. Sterne

It is known experimentally that the refractory metals tantalum and tungsten are embrittled by liquid uranium and plutonium, while vanadium is not.¹ Niobium represents an interesting case of a refractory metal that is embrittled by plutonium but not by uranium. This embrittlement is known to be caused by penetration of the uranium or plutonium into grain boundaries.

When a liquid comes in contact with a surface, a wide variety of behaviors are possible. The liquid may wet the surface, promoting rapid diffusion across the surface, which could lead to an enhancement of any grain-boundary diffusion mechanism into the bulk. Alternatively, the liquid could react with the surface to form an interfacial alloy or a buried layer at the refractory metal surface, or it may fail to wet the surface and prefer to cluster instead. All of these effects would tend to compete against diffusion into grain boundaries and will, therefore, influence the observed embrittlement behavior.

To examine the importance of some of these effects theoretically, we used the linear muffin-tin orbital (LMTO) electronic structure method to calculate the energies of refractory metal surfaces with a single layer of plutonium or uranium either on the surface (as in the case of perfect surface wetting) or as a buried layer, where the plutonium or uranium layer is buried beneath an outer layer of the refractory metal. These geometries represent two limiting cases, corresponding to surface wetting and surface reactivity, that are amenable to calculation. The calculations are performed in a supercell geometry with nine layers of atoms separated by a "surface" region five atomic layers in width. The plutonium or uranium atoms are placed on the outer layers for the overlayer geometry and on one layer below that for the buried layer geometry. Previous studies of plutonium on Nb[110] and V[110] surfaces had indicated that the buried layer geometry was lower in energy in those cases.²

Progress

The present work extends the calculations to consider plutonium on Ta[110] and uranium on Nb[110], V[110], and Ta[110] surfaces. In all these cases, the buried layer geometry had a lower energy than the overlayer geometry, indicating that a single layer of uranium or plutonium prefers to react with the surface rather than remain as a wetting overlayer. This preference is most probably caused in part by differences in surface free energies of the actinides and the refractory metals.

The energy differences in Table 1 summarize the results of these calculations. The large energy differences for the vanadium surface may be caused in part by the neglect of atomic relaxation in the calculations. Nevertheless, we expect that these numbers will still remain large after the inclusion of relaxation effects. It is interesting to note that all systems with energy differences less than 1 eV are known to undergo embrittlement due to grain-boundary penetration, while all those above 1 eV show no such embrittlement. A large energy difference may indicate that a strong bond forms between the uranium or plutonium atoms and the refractory metal atoms, promoting the formation of the buried layer. Strong bonding implies reduced surface mobility, which results in reduced diffusion into grain boundaries.

While the observed correlation between energy difference and tendency towards induced embrittlement is suggestive, there are several other mechanisms that have not been considered yet that could also compete in energy with the buried layer geometry, e.g., a surface alloy. We also need to consider the differences between having a surface, which is the case modeled here, and the liquid-solid interface that is really present in the experiments. More work is required to develop the theory to the status of a predictive tool.

Table 1. Energy difference between overlayer and buried layer geometries per uranium or plutonium atom.

Substrate	Plutonium (eV)	Uranium (eV)
V[110]	3.9	8.1
Nb[110]	0.8	1.1
Ta[110]	0.6	0.75

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Molten Salt Destruction of High Explosives

B. E. Watkins, R. S. Upadhye, and R. Behrens, Jr.*

The Energetic Materials Center (EMC), a partnership of LLNL and Sandia National Laboratories, is developing the molten salt destruction (MSD) process as an alternative to the current method of open burning/open detonation (OB/OD) destruction or incineration of energetic materials. The MSD development effort by the EMC is a collaboration with the Department of Energy; the Department of Defense through the Office of Munitions and the U.S. Army Defense Ammunition Center and School; the U.S. Army Armament Research, Development, and Engineering Center; and the U.S. Air Force High Explosives Research and Development Center. We built a bench-scale MSD unit with a destruction capacity of about 1.5 kg of energetic materials/hour.¹ To date we have successfully destroyed pure explosives; explosives formulations, liquid gun propellant (XM46); and orange, red, green, and blue organic, nonexplosive marker dyes and explosives-containing waste sludges from explosives manufacturing plants. In all cases, the destruction has resulted in decomposition products primarily comprising carbon dioxide, water, and nitrogen gas. Less than 1% of the carbon and chemically bound nitrogen in the feed are converted to CO and NO_x, respectively, in all cases.² As a

result of extensive processing experience and experimentation at the bench scale, we designed, fabricated and installed an advanced-design MSD unit with an expected capacity of about 35,000 kg of energetic materials/year.

From the beginning, it was clear that the MSD process is cleaner and more environmentally friendly than other thermal-oxidative destruction processes.² Early data from Rockwell showed that molten salt was capable of scrubbing particulates such as fly ash and acidic gases such as hydrogen chloride, removing the need for post-treatment scrubbing.³ There was also a hint that molten carbonates may possess catalytic properties.⁴ Our work clearly indicates that the MSD process reduces emissions of toxic gases. For example, when the liquid gun propellant XM46 is destroyed in a packed bed incinerator, 48% of the nitrogen in the propellant is released as nitric oxide.⁵ In comparison, 0.46% of the nitrogen emerges as nitric oxide during MSD.⁶ To understand this behavior we investigated the fundamental chemistry of MSD using simultaneous thermogravimetry modulated beam mass spectrometry (STMBMS).

Progress to Date

In our MSD process, we typically charge the crucible with an equal weight eutectic of sodium,

* Sandia National Laboratories.

potassium, and lithium carbonates melting at approximately 400°C. During the course of the destruction process a steady-state condition is established in which the combined concentration of nitrate and nitrite reach a maximum of 8 wt.%.⁷ We previously investigated the kinetics of MSD using a micro-scale molten salt bath and continuous monitoring of the off-gas using mass spectrometry. In a bath of molten carbonates (minimum working temperature of 450°C), the rate of reaction is too rapid to measure. We found that a eutectic of nitrate salts (minimum melting point of 120°C) and eutectic mixtures of alkali metal nitrates and carbonates allow accurate measurement of reaction rates at about 200°C.

The STMBMS apparatus and the basic data analysis procedures have been described previously.^{8,9} Briefly, this instrument allows the concentration and rate of formation of each gas-phase species in a reaction cell to be measured as a function of time by correlating the ion signals at different m/z values measured with a mass spectrometer with the force measured by a microbalance at any instant. In the experimental procedure, a small sample (~10 mg) is placed in an alumina reaction cell that is then mounted on a thermocouple probe seated in a microbalance. The reaction cell is enclosed in a high-vacuum environment ($<10^{-6}$ Torr) and is radiatively heated by a bifilar-wound tungsten wire on an alumina tube. The molecules from the gaseous mixture in the reaction cell exit through a small diameter (0.004 in. for these experiments) orifice in the cap of the reaction cell and traverse two beam-defining orifices before entering the electron-bombardment ionizer of the mass spectrometer where the ions are created by collisions of electrons with the different molecules in the gas flow. The background pressures in the vacuum chambers are sufficiently low to eliminate significant scattering between molecules from the reaction cell and background molecules in the vacuum chambers. The different m/z -value ions are scanned with a quadrupole mass filter and counted with an ion counter. The gas flow is modulated with a chopping wheel, and only the modulated ion signal is recorded. The containment time of gas in the reaction cell is a function of the area of the orifice, the free volume within the reaction cell, and the characteristics of the flow of gas through the orifice.

In this study, two salt mixtures were used: (1) a 37.5:18:44.5 mole mixture of lithium, sodium and potassium nitrates melting at 120°C and (2) a 1:2 weight mixture of this nitrate eutectic and our "standard" 1:1:1 weight eutectic of alkali carbonates. Isothermal experiments were conducted at 200, 210,

and 225°C for each salt mixture. The kinetics of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) destruction were measured. HMX is a common military explosive and the principal ingredient in the main explosive charge in many of this country's nuclear weapons.

Weight loss of HMX from the reaction cell is a good measure of the overall rate of reaction. Figure 1 shows these data at 225°C. These data clearly indicate that HMX decomposes faster in the salt mixture containing carbonate than in the carbonate-free salt. Comparison of weight loss at 200 and 210°C showed a similar trend (data not shown).

Detailed analysis of the evolution of the mass 44 signal was performed using the Kinetics program developed by Alan Burnham.¹⁰ Decomposition of HMX in the nitrate salt was best fit by a single first-order reaction with an activation energy of 47,500 cal/mol and an Arrhenius pre-exponential factor of 6.7 s^{-1} , while decomposition in the nitrate-carbonate mixture showed an activation energy of 43,800 cal/mol and a pre-exponential factor of 6.9 s^{-1} . The drop in activation energy is consistent with the higher reaction rates observed in the salt mixtures containing carbonate. These results suggest that the carbonate in the molten salt has a catalytic effect on the decomposition of HMX.

These data are significantly different than STMBMS decomposition data obtained for pure HMX.¹¹ Pure HMX shows an induction period

Figure 1. Cumulative weight loss of HMX undergoing decomposition in molten salt at 225°C.

followed by an auto catalytic phase. In contrast, these data show that HMX decomposes in molten salt according to a straightforward, single first-order reaction. This is not entirely unexpected because the autocatalytic mechanism relies on decomposition products to be trapped within the crystal matrix. Trapping is not possible in molten salt.

These data support the observations that MSD is a cleaner technology than incineration for the destruction of HMX. Decomposition reactions proceed faster in carbonate salt and lead to more complete combustion with a given residence time. This rate enhancement and the trapping properties of both acid gases and particulates may allow MSD technology to be implemented with a minimum of post-treatment scrubbing.

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Laboratory Directed Research and Development

Exploratory Research

Giant Magnetoresistance Materials with Novel Spacer Layers

A. Chaiken and R. Michel

During the two-year duration of this project, we made important contributions to the fundamental understanding of interlayer exchange coupling in magnetic multilayers. We also introduced to colleagues in the magnetic recording industry the concept of semiconductor-based, giant magnetoresistive devices, an area in which there continues to be great interest. As part of the project we built a completely automated ion-beam sputtering system, vibrating-sample magnetometer system, temperature-controlled magnetoresistance measurement system, and vacuum-annealing furnace. We managed to complete these construction projects and do a lot of science in two years despite the fact that we had very little technical support and had to do almost all the "nuts and bolts" work ourselves. The equipment that we built, the technical expertise that we gained, and the outside collaborations that we developed will all be of use in continuing research on magnetic materials. The ongoing work will include both industrial collaborations and programmatic efforts.

Technical Summary

The main outcome of this project is a detailed understanding of the nature of exchange coupling in iron-silicon multilayers. We find that fundamentally the exchange coupling in these multilayers has the same origin as in metal-metal multilayers like iron-chromium or cobalt-copper, which have been more heavily studied. For example, the exchange coupling in the iron-silicon system is dependent on the thickness of the silicide spacer layer (Figure 1). Here, the $t_{\text{Si}} = 1.4$ nm multilayer has the high saturation field and low remanent magnetization that are characteristic of antiferromagnetically coupled multilayers. The $t_{\text{Si}} = 2$ nm multilayer, however, has a magnetization curve that looks much like that of bulk iron.

There are also important and fascinating differences between the exchange coupling in iron-silicon multilayers and the more commonly studied iron-chromium. These differences are exemplified by the dependence of the coupling on the temperature of the substrate during film growth (Figure 2). Higher

Figure 1. Thickness dependence of exchange coupling in iron/silicon multilayers.

Figure 2. Substrate temperature dependence of exchange coupling in iron/silicon multilayers.

substrate temperatures promote larger antiferromagnetic coupling, suggesting that the occurrence of coupling is related to interdiffusion of iron and silicon.

Figure 3 shows dramatic evidence for the interdiffusion of iron and silicon and the formation of silicide, showing where transmission electron microscope diffraction patterns for an antiferromagnetically coupled and an uncoupled multilayer. These diffraction patterns give striking evidence for the fact that antiferromagnetic coupling occurs only in multilayers with crystalline silicide spacer layers. This finding is of tremendous theoretical importance because it bears directly on the fundamental origin of antiferromagnetic coupling.

Further progress was made in understanding these phenomena when we learned to grow single-crystal iron-silicon multilayers on MgO and germanium substrates. Figure 4 shows high-angle x-ray diffraction patterns for two iron-silicon multilayers. These films were deposited *simultaneously* on the two different substrates but show dramatically different magnetic properties. The differences in exchange coupling can be attributed to the differences in crystallographic texture and perfection. Confirmation of the single-crystal nature of the multilayer on MgO

was obtained using x-ray diffraction equipment at Stanford University.

The metallic nature of the silicide spacer layer in the single-crystal multilayers was dramatically confirmed by electron spectroscopic studies performed at the Advanced Light Source by John Carlisle and Lou Terminello of LLNL. They developed a unique photon-in, photon-out spectroscopy that allows element-specific determination of the valence-band and conduction-band density of electronic states in *buried layers* of multilayers. Figure 5 shows the type of data generated by this powerful new instrument. These iron-silicon multilayer data have instantly settled a controversy that has raged for three years as to whether the silicide spacer layer is a metal or insulator. Figure 5 argues decisively in favor of a metal.

The most time-consuming part of the project was the fabrication of current-perpendicular-to-plane tunnel junctions based on multilayers with silicide and germanide spacer layers. A number of multilayer films have been generated and passed on to our collaborators at NIST/Boulder and Nonvolatile Electronics in Eden Prairie, Minnesota. Figure 6 shows the mask pattern used by NIST to generate tunnel junctions from iron-silicon multilayers and NiFe-Ge-CoCr trilayers. Six 3-in. wafers were sent by LLNL to

Figure 3. Transmission electron microscopy diffraction patterns of two iron/silicon multilayers. The $(\text{Fe}30\text{\AA}/\text{Si}20\text{\AA}) \times 50$ multilayer with an amorphous iron silicide spacer layer and no interlayer exchange coupling. The $(\text{Fe}40\text{\AA}/\text{Si}14\text{\AA}) \times 50$ multilayer has a crystalline B2-structure FeSi spacer and strong exchange coupling. Photos courtesy of Mark Wall, LLNL.

Figure 4. High-angle x-ray diffraction spectra of two $(\text{Fe}40\text{\AA}/\text{Si}14\text{\AA}) \times 60$ multilayers grown simultaneously: (a) a polycrystalline multilayer grown on glass, and (b) a single-crystal multilayer grown on MgO.

NIST, and three 4-in. wafers were sent to Nonvolatile Electronics. Preliminary indications from the NIST fabrication are positive and indicate the presence of giant magneto-tunnelling in the Fe/Si multilayers. NIST is considering continuation of the semiconductor-spacer project in collaboration with Quantum Peripherals CO, Inc., our CRADA partner.

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Figure 5. Near-edge x-ray absorption spectroscopy and soft x-ray fluorescence spectroscopy results taken at the silicon L-edge for a $(\text{Fe}40\text{\AA}/\text{Si}14\text{\AA}) \times 60$ multilayer grown on MgO. Silicon reference data are shown for comparison. Overlap of the conduction-band (dashed line) and valence-band (solid line) density of states for the multilayer shows that the silicide spacer layer is metallic. Data courtesy of John Carlisle and Lou Terminello, LLNL.

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- A. Chaiken, lecturer, 1997 Summer School of the International Center for Condensed Matter Physics, Brasilia, Brazil.
- A. Chaiken, invited talk, 1996 American Vacuum Society Meeting, Philadelphia, PA.
- R. P. Michel, "Experimental Determination of the Electronic Structure of Buried Silicides in Fe/Si Multilayers," 1996 March Meeting, American Physical Society.
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Figure 6. Tunnel-junction lithographic mask pattern generated by collaborators at NIST for patterning of iron-silicon multilayers in integrated-circuit devices.

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- ### Follow-on Funding
- "Advanced Recording Sensor Materials Development," CRADA with Quantum Peripherals CO, Inc., TC-844-94.

Atomic Force Microscopy of Solution-Grown Crystals

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The nanometer-scale morphology of crystalline surfaces has received considerable attention due to the importance of defect-free surfaces, interfaces, and bulk crystals in materials performance. Biological crystals are of particular interest because accurate experimental determination of their structures requires highly perfect single crystals. However, crystallization of proteins and other biological macromolecules is highly problematic, to such an extent, in fact, that it has become the rate-limiting step in most accurate structure analysis.¹ This is true, in large part, because little is known about the growth mechanisms, fundamental materials parameters, and crystalline defects that determine the growth rate and uniformity of such crystals.¹ To understand the mechanisms that control surface morphology, step dynamics, and defect generation in solution-grown crystals, we performed both in situ and ex situ atomic force microscopy (AFM) on single-crystal surfaces. We report results on three systems: the canonical solution-grown crystal KH_2PO_4 (KDP),² canavalin protein crystals,³ and crystals of the Satellite Tobacco Mosaic Virus (STMV).⁴

Canavalin and STMV

Here, we report the first results of in situ AFM on single crystals of the protein canavalin and the virus STMV that reveal two different modes of growth. The results show that growth of canavalin crystals occurs on complex vicinal hillocks formed by multiple, independently acting, screw dislocation sources (Figure 1). On the terraces of these steps, the continual formation of a large number of molecular clusters with diameters of less than ten molecules were observed (Figure 1, inset). Images were obtained that show how these clusters interact with the advancing step and how the cluster distribution evolves with time. While some of the clusters desorb or dissolve on the time scale of imaging, most are stable and have

low mobility. The clusters are incorporated into the advancing steps, as shown by the circled areas in Figure 1, and thus provide a significant fraction of the molecules in the crystal. The clusters appear to be very uniform in size, do not coalesce, and do not grow with time, suggesting that these clusters may have a stable configuration of canavalin molecules and that further additions lead to weakly bound molecules that are energetically unfavorable at these supersaturations.

In contrast to the dislocation growth mechanism of canavalin, STMV was observed to grow by "stack" formation and two-dimensional (2D) nucleation. Surprisingly, no dislocations were observed on any STMV crystals. Figure 2 shows the stack evolution.

Figure 1. A $23 \times 23 \mu\text{m}$ AFM image showing a complex dislocation growth hillock on the canavalin surface. Inset: A $1 \times 1 \mu\text{m}$ area showing clusters on the terraces of the canavalin surface. Note the clusters being incorporated into the step edge in the circled areas.

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The 7.5- μm image in Figure 2(a) was taken early in the experiment. (Note that the micrometer-size particle seen in Figure 2(b) is absent here.) These stacks are formed by three-dimensional (3D) nuclei that land on the surface; 2D nucleation of new islands then occurs on the larger terraces. Once formed, these islands continue to grow outward in the plane and may coalesce with other islands on the same terrace, as seen in Figure 2(b). In Figure 2(c), which was taken at a later time, the step train from another stack is seen to overtake this area.

Fundamental growth parameters were determined for both materials. From the size of the critical radius, the free energy per unit step height of the step edge $\alpha^{5,6}$ is estimated to be less than 0.6 erg/cm² for canavalin and about 0.25 erg/cm² for STMV. From the speed of the steps, the kinetic coefficient for step motion $\beta^{5,6}$ is calculated. The kinetic coefficient itself is a measure of the kinetics of adsorption, diffusion, and incorporation with the rate-limiting step dominating the value of β . For canavalin, we calculate a kinetic coefficient in the range of 0.6 to 2.6×10^{-4} cm/s (depending on pH) and about 6×10^{-4} cm/s for STMV. The kinetic coefficient of elementary steps is about three orders of magnitude smaller in macromolecular biological crystals than in inorganic crystals.⁶ The potential sources for the low value of β in these organic systems include a large barrier to adsorption (shedding the hydration layer), low surface diffusivity, and a low probability that an incoming molecule has the proper orientation for incorporation into the crystal.

A recurring question in macromolecular crystal growth is the nature and influence of incorporated

impurities and the degree to which they affect the quality and properties of the crystals. During the growth of STMV, interaction of steps with a micrometer-size particle was observed. While the particle extended above the surface, as seen in Figure 2(b), the step train simply closed around it. However, following incorporation into the crystal, the former location of the particle became a micrometer-size hole as the steps wrapped around its former location without covering the top surface leading to the formation of a hollow channel (Figure 2(c)). These types of holes were also observed during growth of canavalin and KDP. At high supersaturations of canavalin and STMV the continual incorporation of microcrystals that land on the surface was observed (Figure 3). This process results in extreme distortion of the lattice and the formation of "mosaic blocks" and planar defects and ultimately leads to poor crystal and diffraction quality.

KDP

Growth of the (101) face of tetragonal KDP crystals typically occurs by step-flow on anisotropic tri-pyramidal hillocks formed by dislocation-induced, 0.5-nm monomolecular steps.¹ All dislocations exhibit hollow cores whose circular cross sections are consistent with an isotropic step edge energy. The core radii are in good agreement with theoretical predictions.⁷ We found that the presence of hollow dislocation cores has important implications on growth theory in that it strongly affects the hillock slope and the growth rate. The relationship between the slope of the sector of the hillock and the supersaturation σ is given by

Figure 2. AFM images showing the nucleation, growth, and coalescence of islands and the expansion of the "stack". (a) A $7.5 \times 7.5 \mu\text{m}$ image of the stack in its early stages ($t = 0$). (b) A $25 \times 25\text{-}\mu\text{m}$ image showing 2D nucleation, coalescence, and growth of the stack ($t = 1840$ s). (c) The particle has been incorporated into the growing crystal as the step train from another stack sweeps over resulting in the subsequent appearance of a near micrometer-size hole in the surface ($t = 5,860$ s).

$$p_i \sim b/(l_c + L_i) , \quad (1)$$

where b is the size of the Burgers vector and $l_c \sim 1/\sigma$ is the critical length of the 2D nuclei.⁸

We modified the formula to include the fact that the spiral must turn around the circular hollow core of radius r_0 . We also modified L_i , the linear dimension of the dislocation source, to take into account the fact that while the spiral is turning around the circular hollow core, the shape of the 2D nuclei remains triangular:

$$L_i = r_0 \sum_i \left(\frac{2 \sin(\phi_i/2)}{b_i} \right) , \quad (2)$$

where b_i is the kinetic coefficient of that sector.

Figure 4 shows the relation of p_i vs σ . The solid lines are calculated using the values of the hollow cores measured in our experiments for the value of r_0 and using L_i as described above. The symbols show the measured values of the slopes. The fact that L_i is never equal to zero, even for $b = 1$, means that there is nonlinear dependence of slope on supersaturation. As the critical radius becomes smaller with increasing supersaturations, the value of L_i becomes more important until it dominates at high supersaturation, causing the slope to reach a limiting value.

Figure 3. A $50 \times 50 \mu\text{m}$ image showing the incorporation of microcrystals on the canavalin surface.

Diffusion of monomer and the process of Ostwald ripening⁹ has been observed to occur in air (Figure 5). In this figure, the process of island coalescence, island dissolution, step smoothing and spiral equilibration are all observed to occur over the time period of many days. The rate of island dissolution increases with a decreasing radius, in accordance with the Gibbs–Thomson effect,⁹ and the change in radius exhibits a cubed dependence with time, indicating mass transport is limited by diffusion kinetics.⁹ Several factors indicate that surface diffusion is also important during growth as demonstrated in the following discussion.

The observed step homogenization is a process facilitated by surface diffusion, indicating that this is an important process during growth. The circular core shape of the dislocations indicate that the step edge energy is isotropic and the anisotropic kinetic coefficient for step motion is responsible for the hillock shape. Two of the step directions of the hillock are the same. If bulk diffusion were the only important process, these two sectors would have the same slope and they do not. Previously, it was proposed that a difference in jump distance could be responsible for the anisotropy.⁸ However, we find that monomer can reach all three step directions by a series of short jumps, indicating that the only anisotropy is in the bond distribution along the diffusion path. All of these pieces of information strongly suggest that surface diffusion is an important process during the growth of KDP.

Figure 4. A plot of p vs σ for KDP. The solid lines are calculated from theory, and the symbols are measurements of the slope at various supersaturations.

Figure 5. These two $10 \times 10 \mu\text{m}$ images were taken 188 h apart and show the process of Ostwald ripening, island dissolution, coalescence, and step smoothing due to atom diffusion in air on the KDP surface.

In situ measurements show that at very low supersaturation ($\sim 0.1\%$), growth is a discontinuous process characterized by hesitation due to step pinning by impurities and particles followed by release from pinning sites (Figure 6). From the velocity of the unpinned steps, we determine the kinetic coefficient, $\beta = 200 \mu\text{m/s}$, and from the curvature of the pinned steps, we calculate the step edge energy, $\alpha = 37 \text{ erg/cm}^2$.

These AFM experiments provided considerable insight into the mechanisms that control the growth and limit the quality of solution-grown crystals.

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Matrix-Assisted Laser Desorption–Ionization: Using Time-of-Flight Mass Spectrometry to Identify Biological Molecules

Donald Eades and Hugh Gregg

Matrix-assisted laser desorption–ionization (MALDI) mass spectrometry (MS) is a relatively new technique in analytical mass spectrometry. This potentially revolutionary method was developed in response to the needs of the biotechnical research community who require molecular weight information of picomole to femtomole levels of intact, high mass, and thermally labile macromolecules. While most other analytical MS ionization techniques cause fragmentation, decomposition, or multiple charging, MALDI efficiently places intact macromolecules into the gas phase with little fragmentation and/or rearrangement.

Our project had three primary objectives: (1) to bring the MALDI capability to LLNL, (2) to use the technique as a powerful tool for biotechnical and analytical chemistry research, and (3) to initiate fundamental studies of the MALDI process to better understand analyte–matrix interactions. To meet these objectives, a retired time-of-flight (TOF) instrument was adapted for MALDI analyses, collaborations were established with three research groups in the Biology and Biotechnology Research Program (BBRP) at LLNL, and relevant parameters influencing the MALDI process were identified for further study (i.e., matrix molar absorptivity, sample crystal preparation).

The MALDI procedure is accomplished by mixing the macromolecule of interest with a high molar excess (1:100 to 1:10,000) of an organic matrix that readily absorbs energy at a wavelength corresponding to a ultraviolet (UV) laser.^{1,2} The mixture is dried to form crystals, and upon laser irradiation, the matrix absorbs the majority of the energy, desorbs from the surface, and gently releases the intact analyte into the gas phase. Once in the gas phase, ion–molecule reactions between the excited matrix and the neutral macromolecules generate ionized analyte species that can then be focused into a mass spectrometer for

detection. Because of the compatibility with pulsed techniques (i.e., lasers) and an “infinite” mass range, a TOF mass analyzer typically is coupled to a MALDI source. The resulting MALDI–TOF MS spectra consist of abundant low mass-to-charge (m/z) matrix ions and characteristic molecular weight ions corresponding to the macromolecule of interest.

Although MALDI has proven to be an efficient means of generating intact gas-phase macromolecular ions, the exact mechanisms responsible for its tremendous success remain unclear. One current belief is that both solid- and gas-phase processes contribute to its success. In the solid phase, the process of sample crystal formation (and choice of organic matrix) appears to significantly influence analyte ion production.³ Once desorbed and in the gas phase, ion–molecule reactions appear to be responsible for ionization, and the efficiency of the ionization appears to depend on both the matrix and analyte species.⁴ Because of the uncertainty in the fundamental MALDI mechanisms, the process of selecting appropriate matrices for specific applications remains a trial-and-error approach and, therefore, warrants further study.

Progress

Once adapted for MALDI analyses, the instrument was used successfully to generate MALDI mass spectra of a series of peptides synthesized by the BBRP. These compounds were used for our initial fundamental studies into the influence of matrix material on the production of peptide signal. Based on the current literature of the MALDI technique, ten organic compounds showed the most promise as useful matrices at various laser wavelengths. A UV spectrum was acquired for each compound and the molar absorptivity calculated at 266 nm (i.e., the fourth harmonic of the Nd:YAG laser used) to identify matrices that would be compatible with our laser

system. The compounds exhibiting the highest molar absorptivity were used to generate MALDI spectra of the peptides. The matrices used and their respective molar absorptivity at 266 nm were (1) 4-hydroxy-3-methoxy benzoic acid (9360), (2) nicotinic acid (2180), and (3) 2,5-dihydroxy benzoic acid (540).

The results from this matrix comparison study suggested no clear correlation between molar absorptivity and peptide ion signal. Interestingly, peptide signals were generated with 2,5-dihydroxy benzoic acid, which exhibited much lower absorptivity at the laser wavelength than the other two matrices (i.e., 20-fold less than 4-hydroxy-3-methoxy benzoic acid and 4-fold less than nicotinic acid). This result was not expected based on the current understanding of the MALDI mechanisms (i.e., the matrix must absorb readily at the laser wavelength). Conversely, 4-hydroxy-3-methoxy benzoic acid, which exhibited the highest molar absorptivity at 266 nm, did not generate any detectable levels of peptide signal. These results suggested that other factors contributed to the successful generation of MALDI peptide spectra. One factor that may explain the observations is the compatibility of the analyte and matrix in the solid phase (i.e., crystal preparation). Indeed, we observed improved signals based on rapid crystal formation. Investigations into crystal preparation techniques are scheduled for FY 1996. A more comprehensive and quantitative correlation between matrix and analyte ion signal is ongoing.

The peptide series used above was also used to characterize the system for sensitivity, useful mass range, and mass resolution. Results from these studies indicated peptide sensitivities between 50 and 100 pmol, a useful mass range of up to 2000 Da, and a mass resolution of approximately 100 (i.e., $m/\Delta m = 100$, where m is the mass-to-charge ratio of the ion). In addition, abundant low-mass matrix ions dominated the mass spectra. Because one objective of this project was to use this technique for "real" biological applications, the sensitivity requirement would need to be between 1 and 20 pmol, the useful mass range of this instrument needed to be up to 200 kDa, and unwanted low-mass ions needed to be eliminated. To meet these needs and address the other objectives of the project, the instrument was redesigned to serve as a research-grade instrument dedicated to MALDI investigations.

The instrument was reconfigured for improved MALDI capabilities. The flight path was converted to a linear design, the source was upgraded to a high-voltage, two-stage acceleration region with improved ion optics, and the detection system and data acquisition methods were upgraded. Results from repeating the characterization studies with the peptide series on the redesigned system showed significantly higher sensitivity (5–10 pmol) and the ability to completely remove abundant, interfering, low-mass matrix ions. The system exhibited resolution comparable to other linear TOF systems (i.e., $m/\Delta m = 200$); however, the mass range remained limited (<5000 Da). The reason appeared to be due to the original laser (i.e., Nd:YAG) and laser peripherals (e.g., beam attenuator). To determine the cause of the limited mass range and build a more applicable research-grade MALDI instrument, a new nitrogen laser system was installed. The new system is complete with a precise beam attenuator and power meter for accurate experimental conditions. The N₂ laser was directed toward the sample stage via an alternate vacuum flange, thus allowing independent use of each laser system for MALDI studies. Direct comparisons of each laser system (and, therefore, two wavelengths: 266 nm from the Nd:YAG and 337 nm from the N₂ laser) are being conducted in FY 1996.

In conclusion, a MALDI-TOF system has been constructed from an existing instrument and spectra from peptides have been successfully acquired. The system currently allows sensitive detection of biomolecules with masses less than 5000 and is being upgraded for higher mass performance. Applications using this system and fundamental studies of the MALDI mechanisms have been initiated and are under way.

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A Novel Approach to SiC Film Production for Micromechanical and Electronic Components

Alex Hamza, Mehdi Balooch, and Dino Ciarlo

Stoichiometric, crystalline SiC films grown from fullerene precursors can be grown epitaxially at low substrate temperatures (<1100 K). Conventional chemical vapor deposition techniques require reactor and substrate temperatures as high as 1700 K. Because of the very different chemical interaction of fullerenes with silicon and silicon dioxide surfaces, deposition of the SiC film can be made selective, eliminating the need to etch the SiC film to manufacture devices. Etching of SiC is difficult because of SiC's extreme resistance to chemical attack. The scope of the application of SiC films is extremely broad. The mechanical and chemical properties of bulk SiC suggest that micromachines and microtransducers that operate at high temperatures and/or in extremely corrosive environments can be fabricated from SiC films. These micromachines have enormous applications in microchemistry and microbiology, as well as automotive and aerospace engineering, where there is a need for performance at high temperatures.

A modified atomic force microscope (AFM) and a Nanoindenter were used to determine the mechanical

properties of SiC thin films grown from C_{60} precursors. Use of the modified AFM for mechanical property determination is a new capability for LLNL. Hardness was measured by indenting the film with a modified, diamond-tipped, leaf-spring cantilever. The force is determined from the deflection of the cantilever, and the projected area of the indentation is determined from the AFM topographic image. The hardness of the LLNL silicon carbide films is about 26 GPa, more than twice as hard as the silicon substrate.

A conventional silicon nitride tip was used to image the relative friction between (1) SiC and the tip and (2) silicon and the tip. The coefficient of friction for the SiC film was one-half to one-third of the coefficient of friction for the native oxide of silicon. Figure 1 shows one such friction image of a SiC "A" on a silicon substrate.

The elastic modulus of our SiC film was determined using a nanoindenter. The nanoindenter produced a plot of the force or applied load vs displacement or indentation depth. From the unload-

Figure 1. Atomic force micrographs of a SiC "A" on a silicon substrate in (a) topographic and (b) friction modes, in which the torsional deflection of the cantilever is shown. In the panel labeled "trace," the large torsional deflection corresponds to the lighter shades in the image. In the panel labeled "retrace," large torsional deflection corresponds to the darker shades because the deflection and scan is in the opposite direction.

ing portion of this plot and the image of the projected area of the indent (determined by topographic AFM imaging), we calculated about 300 GPa for the elastic modulus of our film (50% higher than the modulus of bulk silicon). We also used an AFM to image the relative stiffness of SiC on silicon vs the silicon substrate.

These results suggest SiC thin films can be used in microelectromechanical systems (MEMS) to enhance their wear properties and improve their operation. We demonstrated the use of this growth technique to fabricate SiC microcomponents. The mechanical properties of these SiC films are more robust than those for silicon, which is currently used in MEMS. SiC films grown from C₆₀ may present an opportunity for MEMS applications that have not been previously considered.

We also determined that the rate-limiting step for the growth of SiC from fullerene precursors is the diffusion of silicon atoms from the substrate to the surface. This is evidenced by a comparison of the kinetics and morphology for film growth for a silicon substrate with low dislocation density ($\sim 1/\text{cm}^2$) to a substrate with high dislocation density ($\sim 10^8/\text{cm}^2$). The growth rate on the high dislocation density surface is slightly faster than on the low dislocation density surface ($\sim 20 \text{ nm/min}$ vs $\sim 15 \text{ nm/min}$ at 1100 K) but, unfortunately, self-limiting at 200-nm film thickness. The removal of silicon from dislocations erodes the substrate under the SiC film such that there is very little substrate for film adhesion.

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Isotope Measurements for Innovative Groundwater Management

G. Bryant Hudson

We are developing new isotope tracer approaches for solving problems in managing groundwater resources. Groundwater is a critical resource for many regions, and it supplies roughly half of California's water needs. Existing tools for groundwater evaluation are limited in their ability to determine age, origin, and chemical evolution of groundwater, yet this information is central to management of the resource. We are using isotope abundance measurements of several elements—especially hydrogen, carbon, oxygen, nitrogen, and the noble gases—to provide accurate determinations of groundwater age and origin.

Our recent work focused largely on a collaborative study with the Orange County Water District (OCWD). The OCWD is widely recognized as one of the nation's premier water districts for pioneering innovative approaches to water resource management. The OCWD essentially believes that there is no such thing as wastewater. With the Water Factory 21, they recycle 15 million gallons of water daily. This water is injected underground to keep seawater from moving inland and to raise storage levels in the groundwater basin (Talbert Gap Injection Barrier). The broad OCWD goal is to provide a high-quality, reliable, and affordable water supply. A critical step in the reclaimed water purification process is the natural degradation of organics during subsurface transport. California Department of Health Services regulations focus on subsurface residence time; in particular, injected recycled water must stay underground for at least one year before production for human consumption. In this work we developed an isotopic fingerprint of the recycled water so we could identify its presence in extracted water at nearby wells. We also applied a novel dating technique for water, tritium-helium-3 dating, and demonstrated its effectiveness for measuring the subsurface residence time of the recycled water. Initial measurements in the Talbert Gap Injection Barrier show ages in nearby monitoring and production wells ranging from about one to three years, all indicating a flow velocity of about

100 m/y. The nearest production well produces 2.5-year-old reclaimed water.¹

This work also revealed fairly high levels of ^3H and ^{14}C in the recycled water, apparently caused by a biomedical waste stream. While the levels of ^3H and ^{14}C are high relative to the background environment, they are not of regulatory concern. They do, however, provide a potential tracer for the chemical evolution of organic compounds. Trace organic compounds are a major concern in recycled water. We are beginning to measure carbon and oxygen isotopes in organic material.

The power and value of our initial work with OCWD exceeded their expectations and led to a work-for-others contract with them for additional work. This was the first new project approved by the OCWD after their recent bankruptcy. In our more recent work, we are addressing additional fundamental concerns about travel times along flow paths and chemical evolution (especially organic compounds) in the subsurface.

Our recent work has focused on conducting our first isotope measurements in the Orange County forebay area where aquifer units are exposed at the ground surface. In the forebay, water is introduced into the subsurface using several lakes (recharge basins). These basins capture water that would normally flow to the Pacific Ocean. These operations are not currently used for reclaimed wastewater.

We are now using isotope abundance measurements to determine flow paths and flow rates of groundwater in the forebay area. This information, combined with groundwater modeling, will provide the basis for using reclaimed water for artificial recharge in this area. The OCWD plans to reclaim 100 million gallons of water per day by the year 2010, with the forebay as the principal location for recharging this water. Preliminary isotope results show that we can use the natural variations in oxygen and hydrogen isotopes to fingerprint the sources of the recharge water; water from the Colorado River is

especially distinctive. Dating using the tritium-helium-3 method has shown several areas with water significantly older than originally expected (10- to 20-year ages compared to 2- to 4-year ages). The isotope results and geological data are being used together to generate a conceptual model of the entire Orange County basin.² In parallel, the Earth Science Department at LLNL is conducting advanced numerical groundwater modeling of Orange County to compare with the more traditional modeling effort being done by the OCWD.

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Meso-Structural Features in High- T_c Superconducting Materials Using Pair Distribution Function Analysis of Neutron-X-Ray Scattering Data

George H. Kwei

Our goal is to study the local structure of superconducting compounds and other interesting materials to better understand the relationship between the microscopic structure of materials and their macroscopic properties. The methods used involve collecting x-ray or neutron scattering data to give pair distribution functions (PDFs) that provide detailed local structural information that does not involve the extensive averaging inherent in crystallographic analysis. The work we have done should help clarify the relationship between the structures of these materials and their properties.

Accomplishments

We have been concerned primarily with changes in both the crystal structure and *local* structure near structural or electronic instabilities of scientifically and technologically interesting materials. This work falls into five classes: (1) "colossal" magnetoresistance materials, (2) high-temperature superconductors, (3) ferroelectrics, (4) intermetallic alloys, and (5) proteins.

Colossal Magnetoresistant Materials

Colossal magnetoresistance (CMR) in the newly rediscovered doped rare-earth manganite perovskites has triggered an avalanche of scientific activity. The potential use of these materials in magnetic recording certainly has not gone unnoticed, but perhaps the primary motivation has been the opportunity to study the very interesting interplay between electronic structure, magnetism, and structural instabilities, much of which is not yet well understood. We have been studying the temperature dependence of the structures of $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A = calcium, strontium, barium) as a function of alkaline-earth dopant and doping level (for calcium).

In all of this work, sample characterization is extremely important. For example, we have been measuring the temperature dependence of the magnetization and resistivity and titrating for the oxygen stoichiometry for all our samples before collecting the neutron scattering data. We have now collected data at a fixed doping level for three different sized dopants (calcium, strontium, barium) and for many

different doping levels for a single dopant type. This information has been analyzed to give us the temporal evolution of the crystal structure, magnetic moment, and local structure, and to compare this to the measured transport properties. Figure 1 shows an example of the volume contraction at the metal-insulator transition for $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$.

The changes in the bond lengths and bond angles are even more intriguing and are being studied in the context of the Jahn-Teller distortions and charge delocalization. We also studied the local structure and find additional interesting results.

Recently, it was also discovered that CMR exists in the closely related pyrochlore structure type. We just completed a study of the structure of $\text{Tl}_2\text{Mn}_2\text{O}_7$ to see if one can refine a magnetic moment and to see how much oxygen doping is contributing to the CMR.

High-Temperature Superconductors

One of the issues raised by our earlier work on the low-temperature tetragonal (LTT) to low-temperature orthorhombic (LTO) phase transition in $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ($x = 0.125$ and 0.15), is how the octahedral tilts behave at the higher temperature LTO-high-temperature tetragonal (HTT) phase transition. Our expectation is that the tilts persist locally into the HTT phase, despite the tetragonal symmetry. We have some data around this transition that suggests that this is correct, but more data are necessary. These data have now been collected, and Figure 2 shows the planar lattice parameters. These data are now being analyzed using PDF techniques and we find that our initial suspicions have been confirmed.

The samples prepared above have been used in a series of planned neutron recoil experiments where the broadening of nuclear resonances as a function of temperature provides additional information about possible structural instabilities alluded to in our PDF work. Earlier work showed an increase of the lanthanum phonon energy at all temperatures for superconducting $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ when compared with nonsuperconducting $\text{La}_{1.875}\text{Ba}_{0.125}\text{CuO}_4$. Further studies with much thicker samples, sensitive to the weaker barium and copper resonances as well, have been carried out, and the data will be analyzed in the near future.

In 1994, we collected neutron scattering data for the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system over a large range of $x = 0$ to 0.3 , where phonon dispersion curves indicate that the HTT to LTO phase transition follows a *soft mode* behavior. We are now analyzing these data to obtain the local structure at sample compositions and temperatures where the tetragonal-to-orthorhombic phase boundary appears to coincide with the boundary separating superconducting and semiconducting behavior.

We collected neutron scattering data for $\text{YBa}_2\text{Cu}_3\text{O}_7$ made with pure isotopes of ^{63}Cu and ^{65}Cu (which have the strongly differing neutron scattering lengths of 6.43 and 10.61 fm, respectively). This will allow us to obtain the copper *differential* PDFs (DPDFs) involving only pairs with copper and provide much more detailed information about the dependence of local structure—especially the copper-oxygen axial bond on temperature—without contributions from uninteresting pair-correlations (such as

Figure 1. Cell volume of $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ plotted as a function of temperature shows the volume decrease at about 220 K at the metal-insulator transition.

Figure 2. Planar lattice parameters for $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ near the tetragonal to orthorhombic phase transition. The same data will be used to determine local structural changes.

the yttrium–oxygen bonds) to the PDF. The initial results seemed encouraging, but the samples differed slightly in oxygen content. Those initial samples have been reannealed by David Hinks at Argonne National Laboratory, and additional data have been collected. Unfortunately, we have not yet had time to look at these data.

Ferroelectrics

We are beginning to explore the feasibility of using resonant x-ray scattering to obtain contrast between given atoms to obtain DPDFs. In this case, resonant scattering can provide an x-ray scattering factor nearly one-third smaller at small scattering angles and an even much greater contrast at large scattering angles. Initial studies of the rhombohedral-to-orthorhombic phase transition in KNbO_3 show some promise, but detailed analysis remains to be done.

Intermetallic Compounds

In our studies of the intermetallic heavy fermion compound $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$, we noticed strong diffuse streaks in the single-crystal diffraction patterns indicative of crystalline disorder (Figure 3). Thus, we thought it might be an interesting candidate for a PDF study. However, as we probed further into the structure of this material, we discovered that the disorder resulted from stacking faults from the Ce_2Ga_3 layers that are separated by 0.825 nm. Thus this system will provide a unique opportunity to study interactions in quasi-two-dimensional layers of rare earths. Because we were able to solve the structure completely using crystallographic techniques and found no local structural disorder, we will look for another intermetallic alloy for local structural studies.

Proteins

Traditionally, the structure of large biological molecules has been determined using x-ray absorption spectroscopy (XAFS) or high-resolution nuclear magnetic resonance (NMR) techniques over short length scales or by growing the analogous crystals and solving the full structure using x-ray crystallography. In this brief note, we report initial studies of determining the structure of a model compound using PDF techniques that may provide information over longer length scales without the need for solving the structure of a single crystal of a peptide or protein. This technique should be generally applicable to biological molecules in solution. The only requirement is that there be a heavy metal center such as molybdenum, ruthenium, silver, or cadmium.

The PDF is obtained from the x-ray scattering structure factor by Fourier transformation and is equivalent to a Patterson map; it gives the distribution of all pair correlations as a function of the distance between pairs. It is possible to take advantage of the substantial change in the x-ray scattering factor for a given atom at its absorption edge to take differences between PDFs to give radial distribution functions about that atom. This information from a DPDF is equivalent to the information obtainable in an XAFS experiment, but it extends to much longer length scales (i.e., 2.0 or 3.0 nm, instead of 0.5 nm). It should be possible to use DPDF to explore the structure of binding sites in peptides and proteins and to study the changes in these sites. An even more exciting possibility is the accessibility of the tertiary structure of proteins. Because the data will extend to large enough distances, the amino acid sequence can be used with efficient stochastic procedures to test various conformations against the measured DPDF until the correct tertiary structure is found.

Because cadmium has a K-absorption edge at high enough energies (26.711 keV) to allow the collection of x-ray scattering data over a large range of momentum transfer, we concentrate our initial efforts on model compounds of the type $[\text{Cd}(\text{S-cys})_x(\text{N-donor})_{4-x}]$, e.g., cadmium bound to cysteine and histidine-like residues, which may serve as analogs to a large number of zinc binding peptides and proteins ranging from the

Figure 3. Diffuse scattering in $\text{Ce}_2\text{Pt}_6\text{Ga}_{15}$. A slice through the reciprocal space coverage of one histogram. Plotted are the 20 l , 31 l , and 40 l lattice rows showing the diffuse scattering along 7/3, 1/3, l ; 8/3, 2/3, l ; 10/3, 4/3, l ; and 11/3, 5/3, l . The upper and lower edges of the plot field are limited by the edges of the detector. Contours are at arbitrary values of 1, 2, 4, 8, etc.

phytochelatins, to the metallothioneins, and to the major class of "zinc finger" proteins. A number of compounds of this family have recently been synthesized and their structures determined from x-ray crystallography. For our initial study, we collected on and off the cadmium resonance for $[\text{Cd}(\text{S-2,4,6-Pr}_3\text{C}_6\text{H}_2)_2(\text{py})_2]$. These data are now being analyzed.

Future Plans

We plan to continue our DPDF studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) and begin the study of other CMR materials. We also plan to begin a number of studies of the phonon densities of states of some metallic glasses and differential phonon density of state of YBCO.

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Superplasticity in Aluminum Alloys

T. G. Nieh

The most effective way to increase automobile mileage while decreasing emissions is to reduce vehicle weight. A vehicle weight reduction would not only result in huge oil-gasoline savings but also cause a significant reduction in emission. Traditional vehicle body manufacturing technology using stamped sheet steel components cannot be sufficiently improved to meet future vehicle requirements because of the inherent weight of steel and the high cost and long time necessary for stamping tool development. Aluminum has only about one-third the density of steel, and most commercial aluminum alloys possess substantially higher specific strength than steel. Aluminum is also readily recyclable.

There are, however, several obstacles to the introduction of aluminum sheet components. Obstacles include the relatively high cost of aluminum compared to steel, and the forming limits of aluminum are significantly lower than those for steel. As a result of this, there is growing interest in superplasticity, particularly high-rate superplastic forming to form auto body components.¹ These techniques have the advantages of delivering exceptional formability, potentially giving good dimensional tolerance and delivering rapid time to market. Our objective is to develop a basic understanding of high-strain-rate superplasticity in aluminum alloys. Specifically, we will emphasize 2000-series aluminum, one of the primary sheet alloys used to form automobile bodies.

Materials and Microstructure

We chose two alloys for this study to investigate the effect of zirconium addition on microstructure and tensile properties of 2036 Al alloy. The first alloy is the conventional 2036 Al (composition in weight percent: Al-2.72Cu-0.44Mg-0.27Mn-0.27Fe-0.29Si) and the second is 2036 Al with a 0.21-wt% Zr addition (Zr-2036 Al). Both alloys were cast as 75 × 600 × 900 mm rectangular billets. We used a particle-simulated nucleation (PSN) process to produce a fine-grained structure.² The process involved first to hot-forge the cast alloys to 15 mm thick and then roll to 5 mm thick. The forging and rolling temperatures were 500 and 450°C, respectively. The rolled plates were further

annealed (i.e., solutioned) at 480°C for 4 h; the plates were then aged in a furnace with the temperature gradually being increased from room temperature to 380°C in 20 h. (The latter aging step induces the formation of micrometer-sized Al₂Cu precipitates.) After aging, the plates were additionally cold-rolled to about 2 mm thick, from which tensile samples were machined.

The PSN produces a uniform distribution of fine Al₂Cu precipitates in both alloys. However, despite the addition of a 0.21-wt% Zr, experimental results showed that an insignificant difference exists between the aged microstructures (e.g., grain size and morphology) in the two alloys. Figure 1 shows optical photomicrographs of the aged alloys. The aging treatment results in the formation of 100 to 300 nm Al₆Mn precipitates at grain boundaries and Al₂Cu precipitates in grain interiors. The morphology of the grain boundary precipitates is often lens-shaped, while the intragranular precipitates vary from slightly elongated cubes to laths. Figure 2 represents a bright-field-dark-field pair of intragranular Al₂Cu precipitates. The small particle is 180 nm long by 100 nm wide and the larger precipitate is 340 nm long × 160 nm wide. The average Al₂Cu spacing is 900 nm. Very fine Al₃Zr precipitates (20 to 60 nm) are also observed in the zirconium-modified alloy. However, these precipitates are detected mainly within grain interior, rather than at grain boundaries, suggesting they are ineffective in pinning grain boundaries.

Figure 1. Microstructure of (a) 2036 Al and (b) Zr-2036 Al after aging treatment.

Figure 2. Al_2Cu precipitates in 2036 Al: (a) bright-field image and (b) dark-field image. The small particle is 180 nm long $\times$ 100 nm wide and the larger particle is 340 nm long $\times$ 160 nm wide.

Mechanical Properties

Figure 3 shows the steady-state flow stress at 475°C plotted as a function of strain rate for the two alloys. Despite a slight difference in flow stresses, the strain-rate-sensitivity exponent m is similar in the two alloys. A similar observation was also made at 450 and 500°C. Specifically, the m value ranges from 0.13 to 0.19 for 2036 Al and 0.14 to 0.17 for Zr-2036 Al. This result indicates that the 0.21-wt% Zr addition is insufficient to produce an appreciable effect on the high-temperature deformation in 2036 Al. The activation energies Q for deformation were determined to be 163 and 178 kJ/mol for 2036 Al and Zr-2036 Al, respectively. These values are close to the activation energy for self-diffusion in Al, 143 kJ/mol.³ The above results suggest a recovery-type mechanism (e.g.,

dislocation climb) is responsible for high-temperature deformation in these alloys.

Figure 4 shows a comparison of total elongation value at 475°C for the two alloys. Within the strain rate range (2×10^{-1} to $2 \times 10^{-4} \text{ s}^{-1}$), elongation appears to increase only slightly with strain rate, indicating it is not a strong function of strain rate. The decreasing elongation at lower strain rates is probably caused by an increase in grain-boundary cavitation; metallographic examination indicates that grain-boundary cavitation becomes prevalent at strain rates less than or equal to $2 \times 10^{-3} \text{ s}^{-1}$. The elongation values for the two alloys are comparable, suggesting again that the addition of a 0.21-wt% Zr to 2036 Al has little effect on the high-temperature ductility.

Figure 3. Comparison of steady-state flow behavior between 2036 Al and Zr-2036 Al at 475°C.

Figure 4. Comparison of elongations vs strain rate for both alloys at 475°C.

Summary

A PSN process was used to refine the grain structure of the alloy. Within the ranges studied for temperature (450–500°C) and strain rate (2×10^{-1} to $2 \times 10^{-4} \text{ s}^{-1}$), 2036 Al exhibits a strain-rate-sensitivity exponent of less than 0.2 and an activation energy of about 163 kJ/mol, indicating that a recovery-type mechanism (e.g., dislocation climb) is responsible for high-temperature deformation. The elongation value is insensitive to strain rate, and the maximum elongation of about 200% was obtained. A 0.2 wt% Zr addition to 2036 Al resulted in the precipitation of fine (20–60 nm) Al_3Zr particles. However, these particles were distributed primarily within grains rather than at grain boundaries and, thus, did not lead to grain refinement. A higher zirconium addition is apparently necessary to enhance the formability of 2036 Al.

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Bonding and Structure of Nanocrystalline Thin Films

Louis J. Terminello

Our goal is to establish and develop core-level, soft x-ray photoabsorption as an analytic tool for determining the bonding and structure of incoherent, or amorphous, thin films with nanoscale (<10 nm) ordering or domains—in particular, boron nitride and carbon thin films. These films are of great interest to the coatings and microelectronics industries and are used as tribological, passivation, and hardening materials in defense-related programs. Unfortunately,

conventional structure-determining tools that are used to characterize most materials are inaccurate when applied to films or clusters that have long-range order, or domain sizes, less than the coherence length of atomic-structure-probing x rays (<10 nm) or the wavelength of bond-sensitive probes (infrared and Raman <100 nm). Only a local atomic structural probe like core-level photoabsorption can measure the actual bonding and structure in these incommensurate-phase materials.

Progress to Date

In FY 1995, we began determining the bond order of light-emitting and conductive polymer films using core-level photoabsorption. These carbon-based materials promise to play a valuable role in flat-panel color displays. However, there are still several technical difficulties in using these materials for these applications, partly because little is known about the fundamental conductive-electronic properties of the materials, in particular, their degradation mechanism. This work was performed at the Advanced Light Source at Lawrence Berkeley National Laboratory (LBNL) using our participating research team's (IBM, University of Tennessee, Tulane University, LLNL, and LBNL) beam line. Using core-level photoabsorption, we have characterized several light emitting MEH-PPV polymer films that were prepared by H. Pakpaz, H. Lee, and G. Fox at LLNL. We evaluated the destructive process that leads to material failure. With this work, we were able to ascertain that the orbitals of the bonding backbone are disrupted by a photo-oxidation pathway. Exposure of the polymers to both light and oxygen is necessary to cause damage to the film. This type of information is useful in understanding why the current technology for making metallic electrical contacts to the film interacts with the polymer, thereby damaging the light emitting polymer panel.

We also measured carbon 1s core-level photoabsorption from carbon and diamond thin films. These experiments were done in collaboration with C. Zuker, D. Gruen, and A. Krauss at Argonne National Laboratory (ANL). The carbon 1s near-edge x-ray absorption fine structure (NEXAFS) from these films were compared to the photoabsorption from carbon standards: graphite (representative of pure sp^2 bonding) and diamond (representative of sp^3 bonding). The results of this comparison helped to determine which growth conditions lead to films of the most desirable mechanical, electronic, and morphological properties. For example, typical films grown using magnetron sputtering exhibited an equal amount of sp^2 and sp^3 bonding, but films grown at ANL using a microwave discharge to extract reactive carbon dimers from C_{60} molecules produced material that was pure sp^3 (diamond) in character. In fact, these films grown from buckyballs have nanometer-scale grain sizes, and structure measurements on these materials using x-ray and Raman techniques gave indeterminate results. Our measurements provided conclusive evidence that these materials were true diamond films that had unique nanoscale dimensions.

Our work characterizing boron nitride powders and thin films was continued this year with new results in determining stoichiometric defects in BN thin films. This work was in collaboration with A. Jankowski of LLNL and G. L. Doll of GM. In earlier work, we developed x-ray absorption as an analytic technique for characterizing the bonding in incoherent films that were grown under varying conditions. We found that the sp^2 and sp^3 content of BN films could be extracted from the photoabsorption; thus, the technologically important cubic phase could be ascertained. Our recent results showed that nitrogen defects in h -BN films manifested themselves as a series of extra peaks in the π^* structure in the boron 1s photoabsorption. We were also able to show that hexagonal BN films grown on silicon substrates by pulsed laser deposition could be converted to sp^3 (cubic) bonding with subsequent ion implantation. The bond order for these incommensurate films could only be probed with the elementally and chemical-state-specific probe NEXAFS.

Summary

Our project for characterizing the bonding and morphology of incoherent thin films has been fortunate to have access to the recently commissioned Advanced Light Source at LBNL. As part of the participating research team, we have begun more bulk sensitive measurements that relate the structure of novel materials to features in the x-ray fluorescence and the core-level photoabsorption. In particular, we initiated the probing of some new novel materials with core-level photoabsorption and soft x-ray fluorescence. These include the characterization of carbon aerogels.

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Selenium Isotope Geochemistry

Alan Volpe and Brad Esser

Selenium pollution will be a prominent water-quality issue in the western United States for many years. High levels of selenium in the environment are linked to increased rates of death and deformity in migratory birds, blind staggers in domestic livestock, and selenosis in humans. In California, agricultural drain waters, oil refinery effluent, and semiconductor industry effluent contribute to high selenium content in the San Joaquin Valley and San Francisco Bay. The importance of these industries to California's economy precludes simple abatement, while the complexity of selenium cycling precludes simple remediation.

Selenium has six stable isotopes. We propose to measure variations in the isotopic composition of selenium in water and soil samples caused by natural processes and to show for the first time the value of isotopic measurements in characterizing selenium pollution. The research seeks to identify sources of selenium pollution, determine processes in the selenium cycle, and support selenium remediation studies. We hypothesize that microbially mediated oxidation and reduction processes will affect both the speciation and isotopic composition of selenium in natural and contaminated systems. This proof-of-principle study may have a profound impact on the field of stable isotope geochemistry.

Our project has analytical and field tasks. Analytical tasks involve development of sample chemistry and mass spectroscopic instrumentation. In the first year, we developed chemistry to extract and purify the various species of selenium found in waters and soils. We use an anion exchange column chemistry that allows us to preconcentrate, separate, and determine low levels of different selenium species, selenite, and selenate in natural waters. Development of this technique included the preparation of selenite and selenate standards, which are useful in isotope dilution and isotopic composition work. Figure 1 shows a column calibration for the anion resin exchange chemistry. In addition, we developed total selenium chemistry that includes organic and elemental selenium. This ability to separate the naturally occurring species of selenium in soil and water samples is essential to understanding selenium isotope fractionation.

This project will provide a new analytical capability called negative thermal ionization mass spectrometry (NTIMS) for LLNL's isotopic measurements. We plan to measure selenium isotopic composition with high precision and accuracy using NTIMS. Currently, there is only one research group in the world (Regensburg, Germany) that performs routine high-precision selenium isotopic measurement. Our first-year efforts focused on converting an existing mass spectrometer from positive to negative ionization capability. This is a challenging task for old-generation instruments that are no longer supported by the commercial vendor. The conversion involves modifying the high-voltage power supply for ion-beam focusing, modifying the source chamber to eliminate electric shorting, switching the magnetic field, and converting the software operating system to modern PC mode. We anticipate that the mass spectrometer will be operational in the early part of the second year.

During the first year, we pursued alternate mass spectrometric measurements of selenium using inductively coupled plasma-mass spectroscopy (ICP-MS) and ion microprobe. The ICP-MS technique measures isotope ratios of solutions with 0.5 to 2.0% precision. This precision is inadequate for unequivocal

determination of naturally occurring selenium isotopic fractionation. Nevertheless, selenium abundances are currently being determined by ICP-MS using external calibration standards with a precision of 2 to 5%. In the second year, we will use isotope dilution to determine concentrations more precisely and accurately. The ion microprobe analyzes selenium isotopic composition in micro solid material with 0.1 to 0.5% precision. Though the precision is better than ICP-MS, the absolute composition of selenium isotopes measured by ion microprobe deviates significantly from reported values. The reasons for these differences are unknown, and we plan no additional tests using this technique.

Our second task is to demonstrate the value of selenium isotopic study to environmental problems. We established a joint project with U.S. Geological Survey scientists that builds on their seminal studies describing the sources and transport of selenium pollution in the San Joaquin Valley. In May, we sampled waters from natural springs in the Panoche Hills on the western side of the valley. These highly reduced and sulfurous waters are a significant source of natural selenium from marine shales that form the Coast Range. Published selenium concentrations in these waters range from 2 to 60 ppb, considerably enriched over typical river concentrations of 0.02 to 0.72 ppb. We determined selenite and selenate in six samples from these springs using ICP-MS and found that abundances range from 0.05 to 44 ppb, with selenate greatly enriched relative to selenite.

Field work in the second year will involve agricultural drain water in the San Joaquin Valley and sediments in north San Francisco Bay and Delta regions. Sediment cores in the north San Francisco Bay show striking demarcation between oxidized and reduced selenium species. We expect that a study combining selenium speciation, selenium isotopic composition, and sediment age will provide unique data relating to process characterization and rate. We plan to seek competitive research funds from multiple agencies to continue this work.

Figure 1. Selenite and selenate column chemistry on AG1-X8 anion exchange resin. This technique effectively separates selenite and selenate with high and reproducible chemical yield. For each of the three calibrations, about 50 mL of a standard solution containing (a) selenite, (b) selenate, or (c) a mixture of selenite and selenate was brought to pH 8 with KOH and passed through 2 mL of resin. Selenite was eluted in 1 N formic acid, while selenate was eluted in 3 N HCl. The column was rinsed with 8 mL of MQ water after the sample solution and after the formic acid. Column cuts were analyzed by ICP-MS with better than 5% precision. The apparent breakthrough during loading of the sample solution (0–48 mL) is not real; it reflects interferences of potassium in the selenium mass region during ICP-MS analysis. The selenite signal in the selenate experiment (56–72 mL) reflects residual selenite in the selenate standard. This standard was prepared by oxidizing a selenite standard.

Enhanced Nuclear Stability

John F. Wild, Ronald W. Loughheed, and Kenton J. Moody

In FY 1995, we continued our collaboration with Russian scientists at the Joint Institute for Nuclear Research (JINR) in Dubna, Russian Federation, by searching for the unknown nuclide $^{273}110$. Over the last decade, nuclear theory has predicted that an enhanced stability against spontaneous fission occurs in heavy nuclei near predicted nucleon shell energy gaps at $N = 162$ and $Z = 108$. This enhancement in stability is caused by the attainment of a sausage-shaped nucleus resulting from the $\ell = 4$ vibration mode. We demonstrated in 1993 that this increase in stability indeed exists by measuring the α -decay properties (α -decay energy and half-lives) of two heavy $Z = 106$ isotopes, ^{265}Sg and ^{266}Sg , that are near but not at the predicted nucleon numbers. The half-lives of these nuclides were several orders of magnitude greater than previous theory had predicted. In searching for $^{273}110$, we wished to determine if the predicted neutron shell energy gap was indeed at $N = 162$ or at a greater number by measuring the α -decay properties of a nucleus with $N > 162$. As is known from previous studies, the α -decay energies for isotopes of a given element decrease monotonically with increasing neutron number N of the isotope until a neutron subshell is crossed, at which point the α -decay energy increases. The magnitude of the increase is a measure of the strength of the closed subshell. With $N = 163$, the isotope $^{273}110$ is a nuclide that would enable us to observe this increase if its neutron number is beyond the subshell (Figure 1).

We produced the isotope $^{273}110$ by bombarding a target of ^{244}Pu with ^{34}S ions at the JINR U400 cyclotron; a gas-filled mass separator attached to the beam line was used to reduce the level of undesired background reaction products by many orders of magnitude. We acquired raw data from 1375 h of bombardment between September 10 and December 31, 1994, with an accumulated beam dose of 2.6×10^{19} ^{34}S ions. We made an extensive search through this data for decay sequences fitting the expected pattern of implantation into a position-sensitive detector and subsequent decay of $^{273}110$ and its descendants. We selected several promising candidate sequences, from which we identified one three-member sequence of α -decays linked genetically in both time and position

that fit the expected sequence for $^{273}110$ very closely. From this sequence, we measured the α -decay energy of $^{273}110$ as 11.35 MeV and its half-life as 0.3 ms. By comparing our result with those for isotopes of $Z = 110$ with $N < 162$, which were obtained concurrently at the Gesellschaft für Schwerionenforschung (GSI) at Darmstadt, Germany, we demonstrated conclusively that the subshell crossing is at $N = 162$. The α -decay energy at $N = 163$ is at least 0.6 MeV greater than would be expected if the neutron subshell were at $N \geq 164$. The magnitude of this increase indicates that the strength of the $N = 162$ subshell is comparable to that for $N = 152$ (Figure 1). Our work, together with the concurrent GSI work, constitutes the codiscovery of element 110.

To continue our work to map out the enhancement of nuclear stability in this region, we also participated in an experiment to study the decay properties of ^{257}No , $^{261}104$, and $^{262}104$ via the bombardment of ^{244}Pu with ^{22}Ne . These nuclides are at the terminus of decay sequences such as those of $^{273}110$ and as yet unknown nuclides with $Z > 110$, and a good knowledge of their decay properties (half-lives, decay modes, and the abundance of each) is essential for confirming the identification of atoms of elements 110 through 114. We searched specifically to find an α -decay branch for $^{262}104$ and an SF branch for ^{257}No , but we could only set limits of 2.5% and 1.2%, respectively, at the 68% confidence interval.

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Figure 1. α -Decay energy Q_α vs neutron number N for isotopes of even Z elements from Fm through $Z = 110$. This graph illustrates the behavior of Q_α as it crosses a neutron subshell.

Laboratory Directed Research and Development

Director's Initiative

Multilength-Scale Modeling: Crystal-Plasticity Models in Implicit Finite-Element Codes

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A multidisciplinary team of researchers from Chemistry & Materials Science, Mechanical Engineering, and Physics recently completed the first year of an LDRD Director's Initiative project. This project involves the development of physics-based, multilength-scale models to optimize casting and deformation processing of polycrystalline materials. The purpose of this initiative is to develop models to simulate a material's mechanical response on the mesolength scale. The mesolength scale refers to the realm where the material microstructure (e.g., grain size and shape, crystallite orientation) is resolved but dislocations are homogenized.

Recent development of two experimental technologies has provided a unique capability to validate material models on the mesolength scale. The first of these technologies is the ultrahigh-vacuum diffusion-bonding machine that was patterned after a similar system built at Stuttgart and subsequently constructed here at LLNL. This machine has been demonstrated to build bicrystals with high-precision planar grain boundaries joining two precisely oriented crystallites.

The second technology is orientation imaging microscopy (OIM),¹ developed at Yale University. This technology has been demonstrated to determine precisely the local lattice orientation in a microstructure. This provides a powerful tool to characterize local lattice rotations following specified levels of deformation. The coupling of these two technologies provides a tool for detailed study of a material's mechanical response due to the presence of an interface or grain boundary.

The first phase of this initiative was to build a bicrystal consisting of two crystallites joined by a single, planar grain boundary. The bicrystal was then deformed by channel-die compression while we

recorded the deformation response. Comparisons were made between the measured response and predictions using a three-dimensional finite-element simulation that uses a crystal-plastic material model.

In this study, we are primarily interested in the deformation response of crystalline solids composed of face-centered cubic (fcc) crystallites. For an fcc system, the deformation is assumed to result solely from shear slipping along close-packed crystallographic planes. By inspecting an fcc unit cell, we saw that it has four unique slip planes, each having three unique slip directions (not counting their negatives). A slip plane together with an associated slip direction constitutes a slip system. Thus, there are a total of 12 slip systems that may operate in the fcc single crystal to achieve a deformation. An arbitrary deformation in a single crystal is achieved by the composite effect of all contributing (active) slip systems.

One objective of our work was to incorporate a tensor-based single crystal constitutive model that includes the kinematics of the crystal's deformation response coupled with a scalar law that relates the shear stress, resolved onto the slip plane and slip direction, with the associated slip rate. From the description of the crystal's deformation response, to achieve plastic slipping on a given slip system the yield criterion must be satisfied according to Schmid's law, which states that plastic slipping initiates when the shear stress, resolved onto a slip system, reaches a critical value.

The constitutive model that was applied falls within the general framework of the finite deformation theory of crystals that has been thoroughly documented in the literature. It assumes that the elastic response of the crystallite is undisturbed by plastic slip, and hence, the plastic deformation of a crystal may then be envisioned as a decomposition into two subsequent deformations: first a homogeneous shearing on a given slip system, followed by the simultaneous rigid body rotation and elastic

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distortion of the lattice. The kinematic description of the crystal mechanics used in the constitutive model follows that presented by Peirce, Asaro, and Needleman² and later adapted for use in the finite deformation code ABAQUS by Becker.³ The model was then adapted for use in LLNL's implicit finite deformation code NIKE3D.

Modeling

To illustrate the behavior of this material model, a finite-element model was produced for a bicrystal with a grain-boundary misorientation specified to induce strain localization near the interface. This was done by selecting respective crystal orientations such that one crystallite would be more resistant to plastic slipping than the other crystallite, thus illustrating strong inhomogeneity of plastic strain due to the misorientation across the interface. A flat planar surface was modeled as the interface between the two crystallites. Each crystallite in the bicrystal was modeled with a $9 \times 9 \times 9$ grid that resulted in 1458 total elements. The deformation was then modeled as a channel-die compression operation by deforming the bicrystal in the direction normal to the grain-boundary interface, constraining it along a transverse dimension and allowing free plastic flow in the third dimension. The simulation was carried out to 30% bulk deformation along the compression direction. The predicted deformation was then stored for comparison with the experiments. During the simulation, lattice deformation history was loaded in a file from which, using polar decomposition, the predicted lattice rotations were obtained as function of grid location. From this information, simulated pole figures were generated for comparison with the experiments.

Experiments

Two bicrystals were constructed identical (within the precision of the instruments) to the geometry used in the finite-element simulation described above using the ultrahigh-vacuum diffusion-bonding machine with high-purity aluminum single crystals. Before the mechanical tests, the surfaces specified to remain unconstrained during deformation (i.e., the free plastic flow surface) were thoroughly characterized using OIM with a 1- μm grid. From these measurements, microtexture information was extracted and the corresponding pole figures obtained. Detailed grain maps were also obtained by generating contrast between two grid points when the absolute angle of misorientation exceeded a specified amount. The two

bicrystals were then deformed in channel-die compression to 10 and 30%, respectively. Teflon tape was used as a lubrication to minimize local surface distortion. The bicrystals were mapped following the deformation for surface topography and surface strain using optical measurements. The free surface of each sample was then mapped again using OIM to determine regions of substructure and localization. From these experiments, pole figures and detailed grain maps were again produced.

Comparison of the calculations with the experiments showed fair agreement for the bulk overall deformation response; e.g., the predicted response of the crystallite in the "harder" initial orientation showed less drastic localization and flow behavior than did the "softer" crystallite. However, the calculated response of the softer material was still stiffer than that shown by the experiment. Also, inspection of the predicted and measured pole figures showed quantitative agreement between the two in some of the stereological locations and poor agreement in other locations. Possible reasons for the lack of agreement include poor image quality from the OIM measurement because of the rough surface topology on the deformed surfaces and oxidation. Also, the finite-element calculations used single-point element integration that can result in a stiffer predicted response. Measures are currently under way to correct some of these problems: Careful surface preparations have been performed, and higher-order integration schemes are being implemented in the simulations.

Future Work

This single-crystal constitutive formulation includes no information about the length scale of the material, geometry or deformation process. Recent work showed strong correlation between plasticity phenomena (e.g., hardening) and material length scale and has suggested the need for more sophisticated plasticity laws.⁴ Such a formulation, based on strain gradient theory, has been developed and is currently being demonstrated for microindentation predictions in isotropic materials.⁵ The size effects that are demonstrated in microindentation tests can be predicted by the strain gradient theory. In the near future, work will include development of a new crystal-plastic model in the context of strain gradient plasticity. Such a model will then be implemented in an implicit finite element code and demonstrated with microindentation calculations on a single crystal. Such calculations will be compared with the results from the conventional crystal-plastic model that was described above. Finally, the results from these

calculations will be directly compared with microindentation experiments on single crystals of copper or aluminum. Correlated with these experiments, the analyses can be used to either confirm or rebut the strain gradient theory. Once a strain gradient theory is successfully implemented in a single-crystal computational scheme, more sophisticated homogenization schemes than are currently available in polycrystal calculations will be needed that include misorientation and morphology of a microstructure. Work is currently under way to develop such homogenization theories.

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Molecular Level Studies of Energetic Materials

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Alloys

Our original intent was to create binary high-explosive combinations at the molecular level. There were momentary visions of new explosives based on multiple binary combinations. However, we found that alloying is not so easily obtained as was hoped. Dinitrobistriazole-aminonitrotriazole (DNBT-2ANTA) has remained the only known, proven alloy and was found at the Naval Research Laboratory by accident. Other pairs of molecules either do not mix at all or mix too well. In the latter case, the molecule with the most nitro groups becomes acidic and has a proton pulled off by the other, more basic compound. This leads to the formation of a salt, which has a low density because of its ionic character. Low densities mean low energy per unit volume, an unacceptable quality in an explosive.

The enthalpies of formation for the DNBT-2ANTA complex and the pure compounds, however, were measured using semimicrocombustion calorimetry. The enthalpies of formation were determined to

be 66.7 kcal/mol for DNBT, 14.5 kcal/mol for ANTA, and 102.4 kcal/mol for the complex. The difference in enthalpy between the starting materials and the complex of 6.7 kcal/mol is caused by the intermolecular hydrogen bonds.

Molecular Dynamics Theory

Two years ago, shock waves were modeled in three-dimensional (3D) argon crystals. Now, the 28-atom HMX (octahydro-tetranitro-tetrazocine) molecule is being routinely run in 3D with up to 20,000 molecules using the massively parallel 256-processor array at the National Energy Research Supercomputer Center (NERSC). Although the semiempirical parameters need to be modified to attain agreement with the measured unreacted shock wave Hugoniot of HMX, the program has succeeded in moving molecular dynamics to the large molecules used in high explosives. Also, voids of up to 1000 molecules were placed in the crystal and shocked, showing large temperature increases of thousands of degrees as the voids collapsed. At present, the 3D molecular dynamics crystals can be shocked but cannot dissociate.

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However, two-dimensional (2D) arrays of up to 100,000 diatomic molecules have been run with the first simple bond breaking. The addition of dissociation of the explosive molecules is the next major step needed in this field.

Heat of Formation

We calculated the heat of formation of the isolated gaseous molecule using MOPAC PM3 (± 5 kcal/mol) and ab initio methods (± 2 kcal/mol). Mark Needels calculated ab initio heats of sublimation with a massively parallel code using the electron density method (as opposed to Hartree-Fock wave functions). Because the ab initio codes take weeks to run, a method was devised to combine parts of the long-code results with faster empirical codes. The result is the combination of the gaseous and sublimation heats to give the final solid heat of formation. This is the first package created that provides heats of formation of new molecules with a likelihood of several percent accuracy.

It is intended that this will be used, along with new density-calculating codes, to find new super-powerful explosive structures that have not yet been synthesized. As an exercise, three mythical compounds were calculated and produced these results (Table 1). Finding a real explosive 30% greater in power than HMX would create a sellable product for the next generation.

Hot Spots

A selection of 40- μm glass microballoons were incorporated into granular pentaerythritol tetranitrate (PETN) and pressed into a solid in which the microballoons were the only major defects. The samples were then struck by a sabot in the gas gun and the speed of explosive initiation was measured. Hot spots are known to accelerate the onset of detonation, and microballoons are often put into commercial

Table 1. Calculations of three mythical compounds as part of an exercise.

Name	Density (g/cm ³)	Heat of formation (kcal/mol)	Performance ($\times$ HMX)
CO Tetramer	1.84	180	1.7
CNO Cage	2.72	132	2.3
Nitrated Wurzitane	2.00	120	1.3

explosives for this purpose. To our surprise, the microballoons did not increase initiation and actually slowed it by the volume of their presence. Although the glass is undoubtedly mismatched with the shock wave in the organic explosive, they still should have been crushed by the shock wave and produced high local temperatures. We now wonder if the large voids of tens of micrometers are ineffective in creating hot spots and that much smaller sizes are needed. The voids that contributed to temperature in the molecular dynamics calculations mentioned above were much smaller in size. Future work will concentrate on trying to find and shoot small microballoons.

Detonation Physics

The detonation temperatures of several transparent explosives were measured from their blackbody spectrum in the optical region. Figure 1 shows the results from nitromethane at different initiation pressures caused by changing the sabot velocity in the two-stage gas gun. The plateau created by the oncoming piston gives a period of time in which a definite measurement can be taken. The lowest detonation point is closest to the 13-GPa curve. All the curves agree at 3900 K, thereby supporting this value as representing a true detonation temperature.

Figure 1. Temperatures of nitromethane at three pressures just above the detonation point. The level microsecond-long plateau is the place to measure. The lowest pressure at which detonation occurs gives the best detonation temperature.

Figure 2 shows the same measurement for single crystals of PETN shot along the insensitive $\langle 110 \rangle$ and the sensitive $\langle 100 \rangle$ directions. The insensitive direction can be detonated only if the initiation pressure equals the detonation pressure. The detonating 34-GPa sample and the sensitive shots all give the same 4200 K, thereby showing that this point is independent of initiation pressure and direction as one would hope it would be. Most interesting are the pauses of low temperature seen in the low-pressure samples, which are clearly cooking in some unknown way.

A fast-gated Raman spectrometer with about 50 time channels was run 2 μ s long for the first time on a detonation. In the first microsecond, sharp vibrational features were seen for nitromethane and the radicals NO_2 at 655, 1402, and 1561 cm^{-1} ; CN at 917 cm^{-1} ; and CH_3 at 1379 cm^{-1} . This supports the generally accepted idea that nitromethane breaks its first bond between the nitro and the CH_3 groups. In the second microsecond, the line spectra vanish and continuum radiation is seen. The Raman spectrometer offers the hope that the initial breakdown bonds may be identified directly.

Publications

C. S. Yoo and N. C. Holmes, "Shock Initiation of Nitromethane," in *Proc. Joint Conf. High Pressure Technology and the APS Shock Compression of Condensed Matter*, Colorado Springs, CO, June 28–July 2, 1993; presented at the APS Shock Compression Conference, Seattle, WA, 1995.

L. E. Fried, "Molecular Dynamics Simulation of Shocks in Porous TATB Crystals," in *Proc. Joint Conf. High Pressure Technology and the APS Shock Compression of Condensed Matter*, Colorado Springs, CO, June 28–July 2, 1993; presented at the APS Shock Compression Conference, Seattle, WA, 1995.

C. S. Yoo, N. C. Holmes, and P. C. Souers, "Detonation in Shocked Homogeneous High Explosives," in *Proc. Mater. Res. Soc. Fall Meeting*, Boston, MA, November 27–December 1, 1995 (in press).

M. F. Foltz, J. Chandler, P. Pagoria, and A. Mitchell, "Enthalpy of Formation of a Hydrogen-Bonded Explosive Complex," *Thermochimica Acta*, to be published.

Figure 2. Measured temperatures of PETN single crystals for (a) the insensitive $\langle 110 \rangle$ direction and (b) the sensitive $\langle 100 \rangle$ direction. The 23-GPa shot in (a) did not detonate. The three others all gave comparable detonation temperatures. The two shots in (b) are underdriven and initiate to detonation.